–Supporting Information–

Cross Metathesis-Assisted Solid-Phase Synthesis of Glycopeptoids

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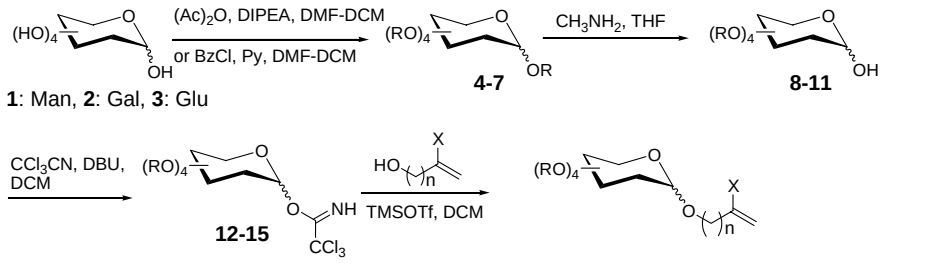
General methods

Chemical reagents were purchased from commercial sources and were used without further purification unless noted otherwise. Moisture sensitive reactions were performed under nitrogen or argon atmosphere. CH_2Cl_2 was dried over calcium hydride. Methylamine was used as 2 M solution in THF for peptoid synthesis and glycine *tert*-butyl ester hydrochloride was neutralized with aq. 1 N NaOH and extracted with DCM prior to use. Grubbs catalyst 1st generation (G1), Grubbs catalyst 2nd generation (G2) and Hoveyda-Grubbs catalyst 2nd generation (HG2) were purchased from Aldrich. Rink Amide AM resin LL (100-200 mesh, 0.4 mmol/g) and TentaGel MB RAM (0.4 mmol/g) were purchased from Novabiochem and Rapp Polymere, respectively. Analytical TLC was performed on Merck 60 F254 silica gel plate (0.25 mm thickness), and visualization was done with UV light and/or by spraying with a 5% solution of phosphomolybdic acid followed by charring with a heat gun. Flash column chromatography was performed on Merck 60 silica gel (70–230 mesh). The ^{1}H NMR and ^{13}C NMR spectra were recorded on a Varian Unity-Inova 500 MHz spectrometer. Me_4Si was used as internal standard for ^{1}H NMR. Reverse-phase HPLC experiments were conducted through an ACE 5 C18-HL (250 x 4.6 mm) reverse phase column on a Shimadzu binary HPLC system equipped with a UV-visible detector at 220 nm. The typical flow rate for analytical HPLC was 1 mL/min. In all cases, a gradient elution of water/acetonitrile with 0.05% TFA was used. Conversion efficiency for CM reactions was determined by HPLC analysis based on the peak integration of glycopeptoid over the total peak integration of unreacted starting peptoid, dimerized peptoid, and glycopeptoid. MALDI-TOF MS was performed on a Voyager-DE STR biospectrometry workstation (Applied Biosystems) with α-cyano-4-hydroxycinnamic acid as a matrix. The peptoids were synthesized in an incubator shaker (JEIO TECH, model SI-600R) or in a microwave oven (Daewoo, model KR-B200R). The microwave reactions were performed at a power of 100 W for peptoid synthesis and at a power of 300 W for CM reactions.

Synthesis of sugar-alkenyl derivatives



4, **8**, **12**: Man(OAc) 4
5, **9**, **13**: Man(OBz) 4
6, **10**, **14**: Gal(OBz) 4
7, **11**, **15**: Glu(OBz) 4

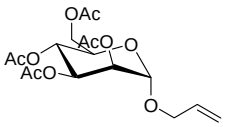
Mannoside
16: R = Ac; X = H; n = 1
17: R = Ac; X = H; n = 2
18: R = Ac; X = H; n = 3
19: R = Ac; X = Me; n = 2
20: R = Bz; X = H; n = 1
21: R = Bz; X = H; n = 2
22: R = Bz; X = H; n = 3
23: R = Bz; X = Me; n = 2

Galactoside
24: R = Bz; X = H; n = 1
25: R = Bz; X = H; n = 2
26: R = Bz; X = H; n = 3
27: R = Bz; X = Me; n = 2

Glucoside
28: R = Bz; X = H; n = 1
29: R = Bz; X = H; n = 2
30: R = Bz; X = H; n = 3

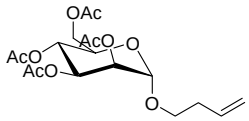
- **General procedure for glycosylation:** To a solution of glycosyl trichloroacetimidate donor (**12**,[1] **13**,[2] **14**,[2a,3] and **15**,[2a,3b] 5.0 mmol) and glycosyl acceptor (allyl alcohol, 3-buten-1-ol, 4- penten-1-ol, or 3-methyl-3-buten-1-ol; 3.0 eq.) in dry DCM (20 mL) was added TMSOTf (0.1 eq.) at –20 °C. The reaction mixture was stirred for overnight. After completion of the reaction, triethylamine (1.0 mL) was added. The reaction mixture was concentrated *in vacuo* to give thick pale yellow oil. Crude product was purified by column chromatography (ethyl acetate: hexane, 1: 9 to 1: 4) to afford compounds **16**–**30** as transparent foamy compounds in 75-90 % yield.

- **Spectral data of sugar-alkenyl derivatives:**

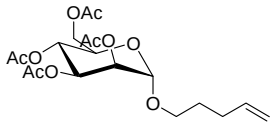


Allyl 2,3,4,6-tetra-*O*-acetate-α-D-mannopyranoside[4] **(16)**: R_f 0.21 (EtOAc–hexane, 1 : 2); ^{1}H NMR (500 MHz, $CDCl_3$) δ_H = 1.98, 2.03, 2.10, 2.14, (12H, s, 4 × OAc), 4.02 (1H, m, H-5), 4.04 (1H, d, J = 5.0 Hz, CH<u>H</u>CH=CH_2), 4.10 (1H, d, J = 11.5 Hz, C<u>H</u>HCH=CH_2), 4.18 (1H, dd, J = 12.5, 4.0 Hz, H-6_A), 4.28 (1H, dd, J = 12.0, 5.5 Hz, H-6_B), 4.86 (1H, s, H-1), 5.20 (1H, m, CH=CH<u>H</u>), 5.25 (1H, d, J = 3.0 Hz, H-2), 5.28 (1H, t, J = 9.9 Hz, H-4), 5.32 (1H, m, CH=C<u>H</u>H) 5.36 (1H, dd, J = 10.0, 3.0 Hz, H-3), 5.85–5.93 (1H, m, C<u>H</u>=CHH). ^{13}C NMR (125 MHz, $CDCl_3$): δ_C = 20.65, 20.67, 20.70, 20.86 (4 × OAc), 62.45 (C-6),

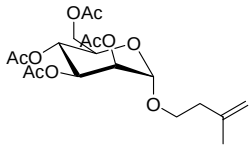
66.18 (C-2), 68.52 (C-3), 68.64 (C-4), 69.61 (C-5), 94.76 (C-1), 118.43, 132.89, 169.71, 169.86, 170.02, 170.61 (4 × OAc).



Butenyl 2,3,4,6-tetra-*O*-acetate-α-D-mannopyranoside (17): R_f 0.24 (EtOAc–hexane, 1 : 2); ^{1}H NMR (500 MHz, $CDCl_3$) δ_H = 1.98, (3H, s), 2.04 (3H, s), 2.09 (3H, s), 2.15 (3H, s), 2.35–2.38 (2H, m), 3.52 (1H, dd, *J* = 15.5, 7.0 Hz), 3.72 (1H, dd, *J* = 17.0, 7.0 Hz), 3.99 (1H, m), 4.11 (1H, d, *J* = 5.0 Hz), 4.27 (1H, dd, *J* = 11.5, 4.5 Hz), 4.81 (1H, s), 5.06–5.13 (2H, m), 5.24 (1H, d, *J* = 3.0 Hz), 5.26 (1H, t, *J* = 9.9 Hz), 5.34 (1H, dd, *J* = 10.0, 3.0 Hz), 5.80 (1H, m). ^{13}C NMR (125 MHz, $CDCl_3$): δ_C = 20.92, 20.93, 20.96, 21.12, 33.93, 62.74, 66.46, 68.01, 68.73, 69.34, 69.89, 97.79, 117.41, 134.57, 170.03, 170.17, 170.34, 170.92. MALDI-TOF: *m/z*: calcd for $C_{18}H_{26}O_{10}Na$ 425.1; found 425.2 $[M + Na]^+$.

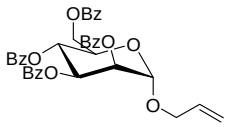


Pentenyl 2,3,4,6-tetra-*O*-acetate-α-D-mannopyranoside[5] **(18)**: R_f 0.44 (EtOAc–hexane, 1 : 2); ^{1}H NMR (500 MHz, $CDCl_3$) δ_H = 1.69–1.73 (2H, m), 1.99, (3H, s), 2.04 (3H, s), 2.10 (3H, s), 2.13–2.15 (5H, m), 3.47 (1H, dd, *J* = 15.5, 5.5 Hz), 3.71 (1H, dd, *J* = 16.5, 7 Hz), 3.97–4.00 (1H, m), 4.11 (1H, d, *J* = 11.5 Hz), 4.27 (1H, dd, *J* = 11.5, 4.5 Hz), 4.80 (1H, s), 4.98–5.06 (2H, m), 5.23 (1H, d, *J* = 3.0 Hz), 5.27 (1H, t, *J* = 10.0 Hz), 5.35 (1H, dd, *J* = 10.0, 3.0 Hz), 5.77–5.83 (1H, m). ^{13}C NMR (125 MHz, $CDCl_3$): δ_C = 20.90, 20.92, 20.95, 21.11, 28.61, 30.38, 62.75, 66.48, 67.97, 68.67, 69.34, 69.91, 97.84, 115.40, 137.93, 169.3, 170.11, 170.30, 170.86.

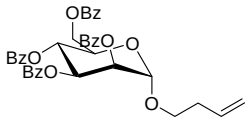


3-Methyl-3-butenyl 2,3,4,6-tetra-*O*-acetate-α-D-mannopyranoside (19): R_f 0.44 (EtOAc–hexane, 1 : 2); ^{1}H NMR (500 MHz, $CDCl_3$) δ_H = 1.75 (3H, s), 1.98, (3H, s), 2.04 (3H, s), 2.09 (3H, s), 2.15 (3H, s), 2.33 (2H, t, *J* = 7.0 Hz) 3.60 (1H, dd, *J* = 15.5, 7.0 Hz), 3.79 (1H, dd, *J* = 16.5, 7.0 Hz), 3.98–4.00 (1H, m), 4.09 (1H, dd, *J* = 13.5, 3.5 Hz), 4.27 (1H, dd, *J* = 12.5, 5.0 Hz), 4.74 (1H, s), 4.82 (2H, d, *J* = 9.5 Hz), 5.22 (1H, d, *J* = 3.0 Hz), 5.26 (1H, t, *J* = 9.5 Hz), 5.34 (1H, dd, *J* = 10.0, 3.0 Hz). ^{13}C NMR (125 MHz,

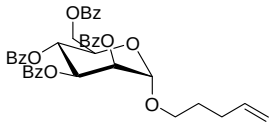
$CDCl_3$): δ_C = 20.91, 20.93, 20.95, 21.13, 22.96, 37.57, 62.76, 66.45, 67.16, 68.78, 69.33, 69.94, 97.74, 112.38, 142.22, 169.39, 170.11, 170.31, 170.87. MALDI-TOF: *m/z*: calcd for $C_{19}H_{23}O_{10}Na$ 439.2; found 439.2 $[M + Na]^+$.



Allyl 2,3,4,6-tetra-*O*-benzoyl-α-D-mannopyranoside[6] (20): R_f 0.53 (EtOAc–hexane, 1 : 2); ^{1}H NMR (500 MHz, $CDCl_3$) δ_H = 4.18 (1H, dd, *J* = 12.5, 5.5 Hz), 4.36 (1H, dd, *J* = 13.5, 5.0 Hz), 4.64–4.51 (2H, m), 4.71 (1H, dd, *J* = 11.5, 2.5 Hz), 5.15 (1H, d, *J* = 2.5 Hz), 5.27 (1H, dd, *J* = 10.5, 1.0 Hz), 5.37 (1H, dd, *J* = 17.0, 1.5 Hz), 5.72–5.73 (1H, m), 5.94 (1H, dd, *J* = 10.0, 3.5 Hz), 5.97–6.04 (1H, m), 6.12 (1H, t, *J* = 10.5 Hz), 7.25–7.60 (12H, m, Ph), 7.83–8.11 (8H, m, Ph). ^{13}C NMR (125 MHz, $CDCl_3$): δ_C = 63.14, 67.19, 69.21, 70.34, 70.79, 96.99, 118.76, 128.54, 128.69, 128.82, 129.20, 129.32, 129.55, 129.96, 129.97, 130.05, 130.09, 133.29, 133.32, 133.42, 133.68, 133.71, 165.68, 165.74, 166.43, 166.65.

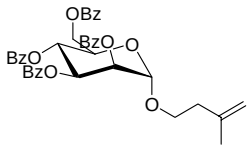


Butenyl 2,3,4,6-tetra-*O*-benzoyl-α-D-mannopyranoside[7] (21): R_f 0.56 (EtOAc–hexane, 1 : 2); ^{1}H NMR (500 MHz, $CDCl_3$) δ_H = 2.49 (2H, d, *J* = 7.0 Hz), 3.66–3.68 (1H, m), 3.86–3.89 (1H, m), 4.46 (1H, m), 4.51 (1H, d, *J* = 12.0 Hz), 4.69 (1H, d, *J* = 12.0 Hz), 5.12 (1H, s), 5.16 (2H, m), 5.70 (1H, t, *J* = 3.0 Hz), 5.91–5.93 (2H, m), 6.10 (1H, t, *J* = 10.5 Hz), 7.25–7.58 (12H, m, Ph), 7.83–8.11 (8H, m, Ph). ^{13}C NMR (125 MHz, $CDCl_3$): δ_C = 34.07, 63.18, 67.22, 68.22, 69.16, 70.36, 70.81, 95.01, 97.88, 117.50, 125.83, 126.73, 128.55, 128.69, 128.83, 129.22, 129.32, 129.57, 129.97, 130.05, 130.09, 133.26, 133.32, 133.42, 133.71, 134.61, 165.71, 165.76, 165.77, 166.44.

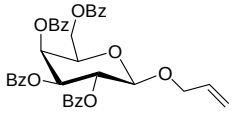


Pentenyl 2,3,4,6-tetra-*O*-benzoyl-α-D-mannopyranoside[8] (22): R_f 0.60 (EtOAc–hexane, 1 : 2); ^{1}H NMR (500 MHz, $CDCl_3$) δ_H = 1.83 (2H, m), 2.22 (2H, m), 3.60 (1H, dd, *J* = 16.0, 6.5 Hz), 3.86 (1H, dd, *J* = 16.5, 6.5 Hz), 4.41–4.45 (1H, m), 4.48 (1H, dd, *J* = 12.5, 5.0 Hz), 4.70 (1H, dd, *J* = 12.5, 2.5 Hz), 5.03 (1H, d, *J* = 10.0, Hz), 5.07–5.11 (2H, m), 5.69–5.70 (1H, m), 5.86 (1H, m), 5.94 (1H, dd, *J* = 10.0, 3.5 Hz), 6.12 (1H, t, *J* = 10.5 Hz), 7.25–7.61 (12H, m, Ph), 7.83–8.11 (8H, m, Ph). ^{13}C NMR (125 MHz,

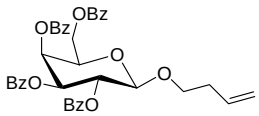
$CDCl_3$): δ_C = 28.75, 30.49, 63.19, 67.26, 68.24, 69.10, 70.34, 70.85, 97.93, 115.51, 128.54, 128.67, 128.82, 129.24, 129.35, 129.61, 129.97, 130.05, 130.09, 130.12, 133.30, 133.40, 133.66, 133.68, 138.02, 165.72, 165.74, 165.76, 166.41.



3-Methyl-3-butenyl 2,3,4,6-tetra-*O*-benzoyl-α-D-mannopyranoside (23): R_f 0.46 (EtOAc–hexane, 1 : 2); ^{1}H NMR (500 MHz, $CDCl_3$) δ_H = 1.81 (3H, s), 2.43–2.46 (2H, m), 3.73 (1H, dd, *J* = 10.0, 7.0 Hz), 3.96 (1H, dd, *J* = 10.0, 6.5 Hz), 4.44–4.46 (1H, m), 4.50 (1H, dd, *J* = 12.5, 5.0 Hz), 4.71 (1H, dd, *J* = 11.5, 2.0 Hz), 4.81 (1H, s), 4.86 (1H, s), 5.13 (1H, d, *J* = 1.5 Hz), 5.70 (1H, m), 5.94 (1H, dd, *J* = 10.0, 3.5 Hz), 6.10 (1H, t, *J* = 10.0 Hz), 7.25–7.61 (12H, m, Ph), 7.83–8.11 (8H, m, Ph). ^{13}C NMR (125 MHz, $CDCl_3$): δ_C = 28.30, 37.69, 63.21, 67.23, 67.44, 69.19, 70.34, 70.86, 97.81, 112.44, 128.53, 128.67, 128.82, 129.24, 129.35, 129.60, 129.97, 130.05, 130.09, 130.10, 133.29, 133.39, 133.66, 133.69, 142.32, 165.69, 165.70, 165.76, 166.41. MALDI-TOF: *m/z*: calcd for $C_{39}H_{36}O_{10}Na$ 687.2; found 687.3 $[M + Na]^+$.

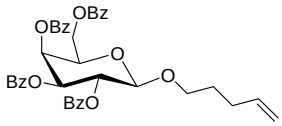


Allyl 2,3,4,6-tetra-*O*-benzoyl-β-D-galactopyranoside (24): R_f 0.55 (EtOAc–hexane, 1 : 2); ^{1}H NMR (500 MHz, $CDCl_3$) δ_H = 4.20 (1H, dd, *J* = 12.5, 6.0 Hz), 4.32 (1H, t, *J* = 8.0 Hz), 4.40–4.52 (2H, m), 4.68 (1H, dd, *J* = 12.0, 7.0 Hz), 4.89 (1H, d, *J* = 7.5, Hz), 5.14 (1H, d, *J* = 11.0 Hz), 5.24 (1H, d, *J* = 17.5, Hz), 5.61 (1H, dd, *J* = 11.0, 4.0 Hz), 5.83 (2H, m,), 6.00 (1H, d, *J* = 3.0 Hz), 7.23–7.62 (12H, m, Ph), 7.77–8.10 (8H, m, Ph). ^{13}C NMR (125 MHz, $CDCl_3$): δ_C = 60.39, 62.04, 68.12, 69.77, 70.29, 71.31, 94.75, 100.23, 118.02, 128.28, 128.37, 128.47, 128.62, 128.74, 128.99, 129.37, 129.41, 129.72, 129.75, 129.77, 130.03, 133.22, 133.28, 133.31, 133.33, 133.60, 165.27, 165.60, 165.71, 166.06. MALDI-TOF: *m/z*: calcd for $C_{37}H_{32}O_{10}Na$ 659.2; found 659.0 $[M + Na]^+$.

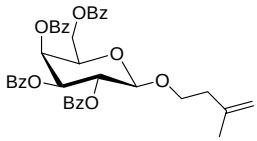


Butenyl 2,3,4,6-tetra-*O*-benzoyl-β-D-galactopyranoside (25): R_f 0.60 (EtOAc–hexane, 1 : 2); ^{1}H NMR (500 MHz, $CDCl_3$) δ_H = 2.29–2.36 (2H, m), 3.64 (1H, dd, *J* = 17.5, 7.5 Hz), 4.02 (1H, dd, *J* = 17.0, 7.5

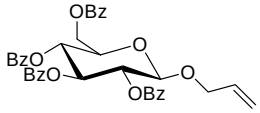
Hz), 4.34 (1H, t, *J* = 6.0, Hz), 4.43 (1H, dd, *J* = 11.0, 7.0 Hz), 4.69 (1H, dd, *J* = 12.0, 7.0 Hz), 4.81–4.85 (2H, m), 4.97 (1H, d, *J* = 15.5, Hz), 5.60 (1H, dd, *J* = 11.1, 4.0 Hz), 5.79 (1H, dd, *J* = 11.2, 7.5 Hz), 5.99 (1H, d, *J* = 4.0 Hz), 6.13 (1H, dd, *J* = 11.0, 4.0 Hz), 7.23–7.65 (12H, m, Ph), 7.77–8.13 (8H, m, Ph). ^{13}C NMR (125 MHz, $CDCl_3$): δ_C = 33.84, 62.01, 68.13, 68.54, 69.45, 69.68, 71.30, 90.68, 101.70, 116.77, 128.33, 128.40, 128.61, 128.74, 128.83, 128.99, 129.28, 129.47, 129.76, 129.94, 130.05, 133.18, 133.29, 133.48, 133.73, 134.26, 165.49, 165.60, 165.7, 166.07. MALDI-TOF: *m/z*: calcd for $C_{38}H_{34}O_{10}Na$ 673.2; found 673.1 $[M + Na]^+$.



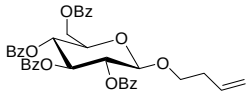
Pentenyl 2,3,4,6-tetra-*O*-benzoyl-β-D-galactopyranoside[8a,9] **(26)**: R_f 0.61 (EtOAc–hexane, 1 : 2); ^{1}H NMR (500 MHz, $CDCl_3$) δ_H = 1.60–1.73 (3H, m), 1.94–2.03 (2H, m), 3.60 (1H, dd, *J* = 16.5, 7.0 Hz), 3.98 (1H, dd, *J* = 16.0, 6.0 Hz), 4.32 (1H, t, *J* = 6.5 Hz), 4.43 (1H, dd, *J* = 10.0, 4.5 Hz), 4.69 (1H, dd, *J* = 12.0, 7.0 Hz), 4.80–4.84 (2H, m), 5.60–5.67 (2H, m), 5.79 (1H, dd, *J* = 10.0, 8.0 Hz), 5.99 (1H, d, *J* = 4.0 Hz), 7.24–7.61 (12H, m, Ph), 7.77–8.10 (8H, m, Ph). ^{13}C NMR (125 MHz, $CDCl_3$): δ_C = 28.55, 29.78, 62.02, 68.15, 69.65, 69.85, 71.27, 71.75, 101.69, 114.91, 128.29, 128.38, 128.46, 128.61, 128.78, 129.04, 129.41, 129.43, 129.70, 129.77, 130.04, 133.22, 133.28, 133.59, 137.72, 165.27, 165.61, 165.82, 166.08.



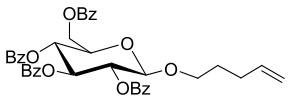
3-Methyl-3-butenyl 2,3,4,6-tetra-*O*-benzoyl-β-D-galactopyranoside (27): R_f 0.60 (EtOAc–hexane, 1 : 2); ^{1}H NMR (500 MHz, $CDCl_3$) δ_H = 1.59 (3H, s), 2.27–2.31 (2H, m), 3.71 (1H, dd, *J* = 17.5, 8.0 Hz), 4.08 (1H, dd, *J* = 15.5, 6.0 Hz), 4.35 (1H, t, *J* = 6.5 Hz), 4.43 (1H, dd, *J* = 11.0, 7.0 Hz), 4.56 (1H, s), 4.60 (1H, s), 4.69 (1H, dd, *J* = 11.5, 6.5 Hz), 4.83 (1H, d, *J* = 9.0 Hz), 5.62 (1H, dd, *J* = 9.5, 2.5 Hz), 5.80 (1H, dd, *J* = 11.0, 8.0 Hz), 5.99 (1H, d, *J* = 2.0 Hz), 7.22–7.61 (12H, m, Ph), 7.77–8.10 (8H, m, Ph). ^{13}C NMR (125 MHz, $CDCl_3$): δ_C = 22.54, 37.36, 62.03, 68.14, 68.70, 69.73, 71.30, 71.75, 101.62, 111.86, 128.28, 128.29, 128.47, 128.61, 128.77, 129.03, 129.43, 129.49, 129.72, 129.77, 129.78, 130.04, 133.16, 133.28, 133.29, 133.59, 141.89, 165.23, 165.42, 165.60, 166.07. MALDI-TOF: *m/z*: calcd for $C_{39}H_{36}O_{10}Na$ 687.2; found 687.3 $[M + Na]^+$.



Allyl 2,3,4,6-tetra-*O*-benzoyl-β-D-glucopyranoside[8a,10] **(28)**: R_f 0.52 (EtOAc–hexane, 1 : 2); ^{1}H NMR (500 MHz, $CDCl_3$) δ_H = 4.15–4.19 (2H, m), 4.37 (1H, dd, *J* = 13.0, 5.0 Hz), 4.50 (1H, dd, *J* = 12.5, 5.5 Hz), 4.63 (1H, dd, *J* = 13.0, 4.0 Hz), 4.90 (1H, d, *J* = 8.0 Hz), 5.11 (1H, d, *J* = 8.5 Hz), 5.23 (1H, d, *J* = 18.0 Hz), 5.56 (1H, dd, *J* = 10.0, 8.0 Hz), 5.68 (1H, t, *J* = 10.0 Hz), 5.76–5.83 (1H, m), 5.91 (1H, t, *J* = 9.0 Hz), 7.25–7.55 (12H, m, Ph), 7.82–8.03 (8H, m, Ph). ^{13}C NMR (125 MHz, $CDCl_3$): δ_C = 63.45, 70.07, 70.34, 72.12, 72.46, 73.22, 100.08, 118.18, 128.54, 138.60, 138.62, 138.66, 129.04, 129.05, 129.55, 129.85, 129.97, 130.00, 130.04, 130.07, 133.39, 133.46, 133.48, 133.55, 133.68, 165.36, 165.46, 166.08, 166.40.



Butenyl 2,3,4,6-tetra-*O*-benzoyl-β-D-glucopyranoside (29): R_f 0.55 (EtOAc–hexane, 1 : 2); ^{1}H NMR (500 MHz, $CDCl_3$) δ_H = 2.28–2.30 (2H, m), 3.61 (1H, dd, *J* = 16.5, 7.0 Hz), 3.97 (1H, dd, *J* = 15.5, 6.0 Hz), 4.14–4.17 (1H, m), 4.51 (1H, dd, *J* = 11.5, 5.0 Hz), 4.65 (1H, dd, *J* = 11.5, 3.0 Hz), 4.82 (1H, d, *J* = 9.0 Hz), 4.87 (1H, d, *J* = 8.0 Hz), 4.94 (1H, d, *J* = 18.5, Hz), 5.53 (1H, dd, *J* = 9.5, 8.0 Hz), 5.65–5.69 (2H, m), 5.90 (1H, t, *J* = 9.5 Hz), 7.25–7.53 (12H, m, Ph), 7.82–8.02 (8H, m, Ph). ^{13}C NMR (125 MHz, $CDCl_3$): δ_C = 34.08, 63.46, 69.71, 70.08, 72.11, 72.45, 73.17, 101.50, 117.00, 128.54, 128.57, 128.61, 128.65, 129.05, 129.07, 129.63, 129.85, 129.98, 130.00, 130.02, 130.07, 133.37, 133.42, 133.47, 133.67, 134.49, 165.33, 165.46, 166.09, 166.41. MALDI-TOF: *m/z*: calcd for $C_{38}H_{34}O_{10}Na$ 673.2; found 673.3 $[M + Na]^+$.



Pentenyl 2,3,4,6-tetra-*O*-benzoyl-β-D-glucopyranoside[9,11] **(30)**: R_f 0.56 (EtOAc–hexane, 1 : 2); ^{1}H NMR (500 MHz, $CDCl_3$) δ_H = 1.57–1.68 (2H, m), 1.93–2.00 (2H, m), 3.55 (1H, dd, *J* = 16.5, 7.0 Hz), 3.93 (1H, dd, *J* = 15.5, 6.0 Hz), 4.15–4.16 (1H, m), 4.50 (1H, dd, *J* = 12.0, 5.0 Hz), 4.65 (1H, dd, *J* = 11.5, 4.0 Hz), 4.80–4.84 (3H, m), 5.53 (1H, dd, *J* = 10.0, 7.5 Hz), 5.60–5.69 (2H, m), 5.90 (1H, t, *J* = 10.0 Hz), 7.25–7.55 (12H, m, Ph), 7.82–8.02 (8H, m, Ph). ^{13}C NMR (125 MHz, $CDCl_3$): δ_C = 28.79, 30.01, 63.47, 69.68, 70.11, 72.18, 72.42, 73.20, 101.52, 115.15, 128.54, 128.60, 128.65, 129.06, 129.08, 129.60, 129.86, 129.98, 130.00, 130.07, 133.36, 133.45, 133.47, 133.67, 137.97, 165.34, 165.46, 166.10, 166.41.

General procedure for peptoid synthesis

Peptoids were synthesized on Rink amide AM resin LL (**31-32**, **37**, and **49**) and TentaGel MB RAM resin (**59**) by the conventional submonomer strategy.[17] Peptoid syntheses were performed in 25 mL standard glass peptide synthesis vessels. The resins were swelled in DMF at 25 ^{o}C for 1-2 h. Then DMF was drained, and the beads were incubated 20% piperidine in DMF for 1 h and washed thoroughly with DMF (8 × 3 mL). The beads were treated with 2 M bromoacetic acid (1.0-1.5 mL) and 3.2 M DIC (1.0-1.5 mL) and irradiated in a microwave oven (100 W) for 3 × 12 sec with shaking for 30 sec after each pulse. The beads were thoroughly washed with DMF (8 × 3 mL) and then treated with primary amines (1-2 M, 2.0 mL) in DMF in a microwave oven (100 W) for 3 × 12 sec with shaking for 30 sec after each pulse. Both acylation and displacement were successively repeated to form the desired peptoid sequences. To prevent inactivation of CM catalyst from free amines, the peptoids were capped with Boc-anhydride (10 eq.) and triethylamine (1.0 mL) in DCM (5.0 mL) and the beads were shaken for 2 h before being washed with MeOH (8 × 3.0 mL) and DCM (8 × 3.0 mL), and left to dry under vacuum for 2 h before CM.

General procedure for solid-phase CM of peptoids and sugar derivatives

- Under microwave conditions

The bead containing peptoids (15 mg) and sugar derivatives (20 eq., 25 mM) were shaken in DCB (1.5 mL) for 30 min. Then 5 mol% CM catalysts were added and irradiated under microwave (300 W) for 4 × 30 sec (total 2 min) with shaking for 30 sec after each pulse. The resin was thoroughly washed with DCM (8 × 3.0 mL).

- Under reflux conditions

The bead containing peptoids (15 mg) and sugar derivatives (20 eq., 25 mM) were stirred in anhydrous DCM (1.5 mL) for 30 min. Then 5 mol% CM catalysts were added and refluxed at 40 °C under nitrogen atmosphere for 8 h. The resin was thoroughly washed with DCM (8 × 3.0 mL).

General TFA cleavage procedure

Glycopeptoid-tethered resin was suspended in a cleavage cocktail (92% TFA/5% H_2O/3% TIS) for 1-2 h. After cleavage solution was removed by blowing N_2 gas, 50% aq. acetonitrile containing 0.1% TFA was added and mixed uniformly. The mixture was filtered through 0.2 μm PTFE filter tip and the obtained solution was directly used for HPLC and MALDI-TOF analyses.

Abbreviations

DMF: *N,N*-dimethylformamide, DCB: 1,2-dichlorobenzene, DCM: methylene chloride, DBU: 1,8-diazabicyclo[5.4.0]undec-7-ene, TFA: trifluoroacetic acid, TIS: triisopropylsilane, TMSOTf: trimethylsilyl trifluoromethanesulfonate, DIC: *N,N'*-diisopropylcarbodiimide, G1: Grubbs catalyst 1st generation, [bis(tricyclohexylphosphine) benzylidine ruthenium (IV) chloride], G2: Grubbs catalyst 2nd generation, [1,3-bis-(2,4,6-trimethylphenyl)-2-(imidazolidinylidene)(dichlorophenylmethylene) (tricyclohexylphosphine) ruthenium], HG2: Hoveyda-Grubbs catalyst 2nd generation [(1,3-bis-(2,4,6-trimethylphenyl)-2-imidazolidinylidene) dichloro(*o*-isopropoxyphenylmethylene)ruthenium], CM: cross metathesis, HPLC: high-performance liquid chromatography, NMR: nuclear magnetic resonance, MALDI-TOF: matrix-assisted laser desorption/ionization-time of flight.

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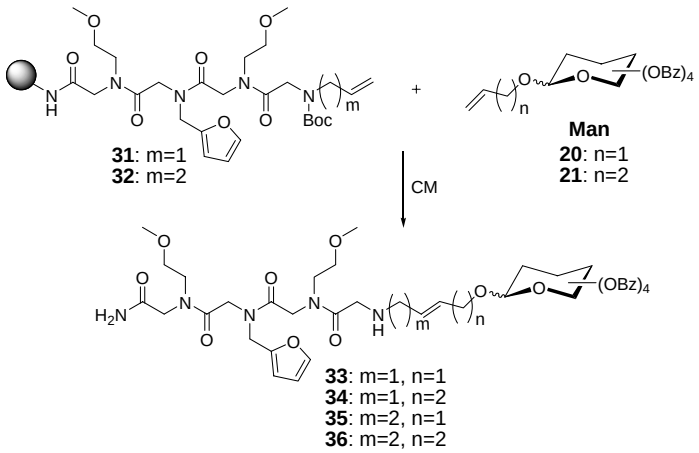
Table S1. MALDI-TOF data of sugar derivatives and (glyco)peptoids.

entry	compound	MS (calcd.)	MS (obs.) ($[M+Na]^+$)
1	**16**	388.1	411.1
2	**17**	402.2	425.2
3	**18**	416.2	439.2
4	**19**	416.2	439.2
5	**20**	636.2	659.3
6	**21**	650.7	673.3
7	**22**	664.7	687.3
8	**23**	664.7	687.2
9	**24**	636.2	659.0

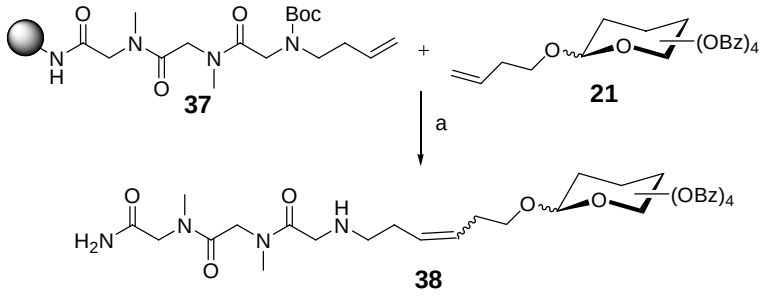
10	**25**	650.7	673.1
11	**26**	664.7	687.2
12	**27**	664.7	687.3
13	**28**	636.2	659.3
14	**29**	650.7	673.3
15	**30**	664.7	687.2
16	**31**	481.3	504.4
17	**32**	495.3	518.2
18	**33**	1089.4	1112.9
19	**34**	1103.4	1126.5
20	**35**	1103.4	1126.3
21	**36**	1117.5	1140.6
22	**37**	270.3	293.2
23	**38**	892.9	915.6
24	**39**	855.4	878.5
25	**40**	869.4	892.5
26	**41**	883.4	906.7
27	**42**	883.4	906.7
28	**43**	1131.5	1154.5
29	**44**	1131.5	1154.5
30	**45**	1103.4	1126.6
31	**46**	1117.5	1140.6
32	**47**	1131.5	1154.5
33	**48**	1131.5	1154.5
34	**49**	642.4	665.6
35	**50**	1250.5	1273.2
36	**51**	1264.5	1287.2
37	**52**	1278.5	1302.5
38	**53**	1250.5	1273.7
39	**54**	1264.5	1287.4
40	**55**	1278.5	1301.5
41	**56**	1250.5	1273.8
42	**57**	1264.5	1287.5
43	**58**	1278.5	1302.0
44	**59**	599.7	622.3
45	**60**	1221.6	1244.5
46	**61**	1235.6	1258.3
47	**62**	1221.6	1244.6
48	**63**	1235.6	1258.3
49	**64**	1221.6	1244.8
50	**65**	1235.6	1258.5

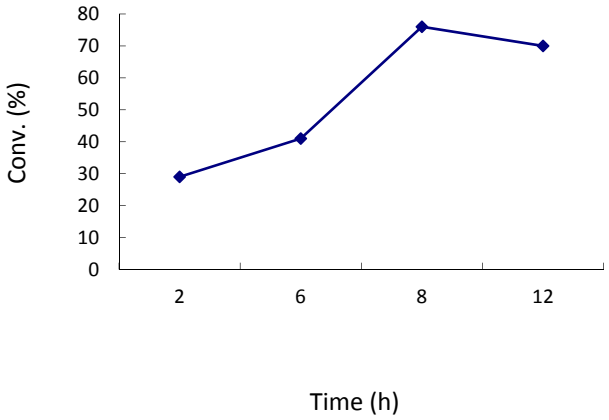
Table S2. Optimization of solid-phase CM.



entry	peptoid	sugar	catalyst	solvent	temp. (°C)	time	product	conv. (%)
1	**31**	**20**	G1	DCM	40	8 h	**33**	<5
2	**31**	**20**	G2	DCM	40	8 h	**33**	<5
3	**31**	**20**	HG2	DCM	40	8 h	**33**	13
4	**31**	**20**	G1	DCB	μwave	3 min.	**33**	<5
5	**31**	**20**	G2	DCB	μwave	3 min.	**33**	<5
6	**31**	**20**	HG2	DCB	μwave	3 min.	**33**	<5
7	**31**	**21**	G1	DCM	40	8 h	**34**	<5
8	**31**	**21**	G2	DCM	40	8 h	**34**	10
9	**31**	**21**	HG2	DCM	40	8 h	**34**	29
10	**31**	**21**	G1	DCB	μwave	3 min.	**34**	<5
11	**31**	**21**	G2	DCB	μwave	3 min.	**34**	<5
12	**31**	**21**	HG2	DCB	μwave	3 min.	**34**	20
13	**32**	**20**	G1	DCM	40	8 h	**35**	10
14	**32**	**20**	G2	DCM	40	8 h	**35**	<5
15	**32**	**20**	HG2	DCM	40	8 h	**35**	27
16	**32**	**20**	G1	DCB	μwave	3 min.	**35**	<5
17	**32**	**20**	G2	DCB	μwave	3 min.	**35**	<5
18	**32**	**20**	HG2	DCB	μwave	3 min.	**35**	<5
19	**32**	**21**	G1	DCM	40	8 h	**36**	18
20	**32**	**21**	G2	DCM	40	8 h	**36**	22
21	**32**	**21**	HG2	DCM	40	8 h	**36**	47
22	**32**	**21**	G1	DCB	μwave	3 min.	**36**	<5
23	**32**	**21**	G2	DCB	μwave	3 min.	**36**	<5
24	**32**	**21**	HG2	DCB	μwave	3 min.	**36**	25

Scheme S1. Relationship between Reaction Time and Conversion Efficiency in Solid-phase CM





Reagents and conditions: a. (i) sugar derivative (20 equiv, 25 mM), HG2 (5 mol %), DCM, 40 °C; (ii) 92% TFA.

^{1}H, ^{13}C NMR spectra of new compounds

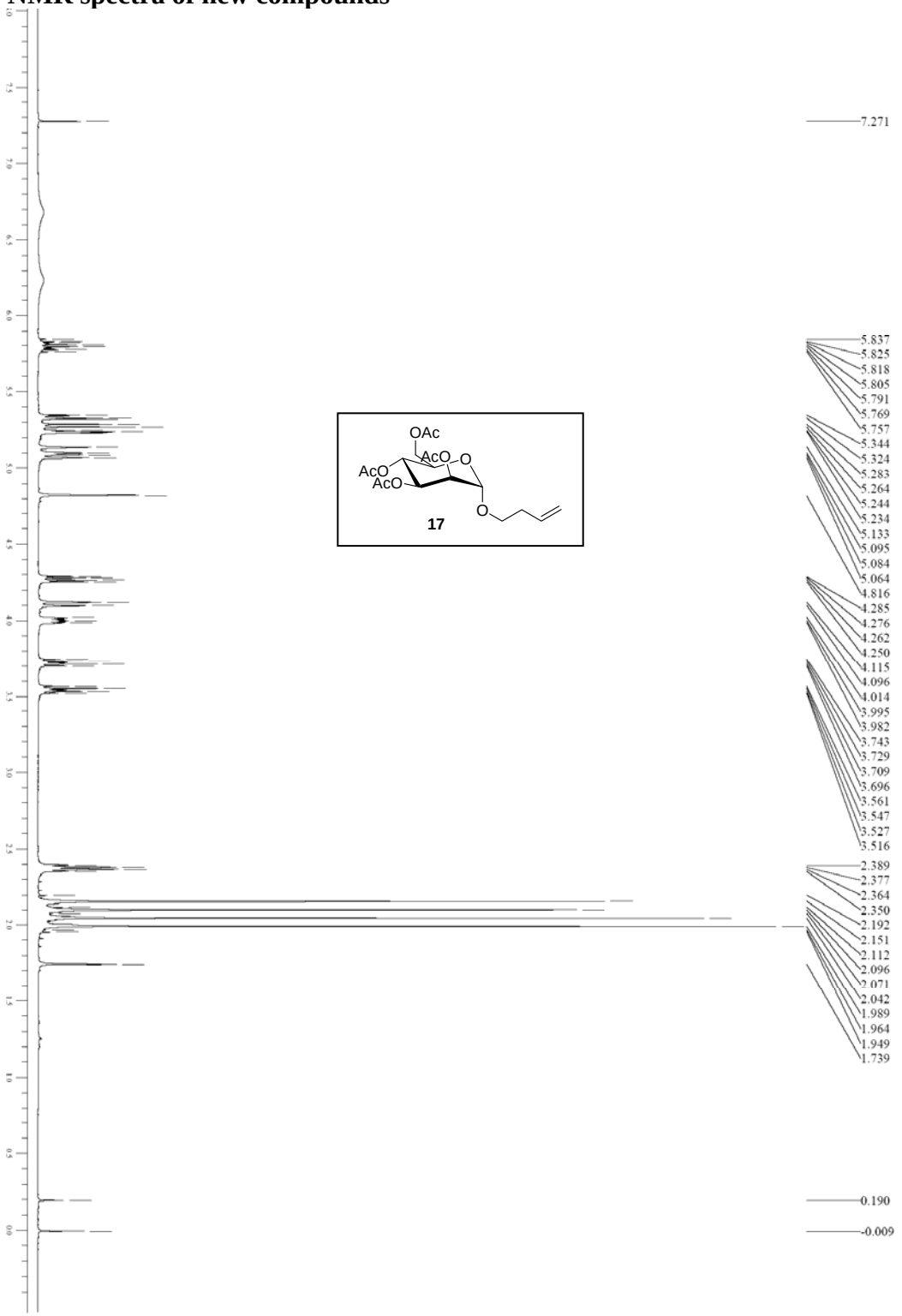


Figure S1. ^{1}H NMR spectrum of compound **17**.

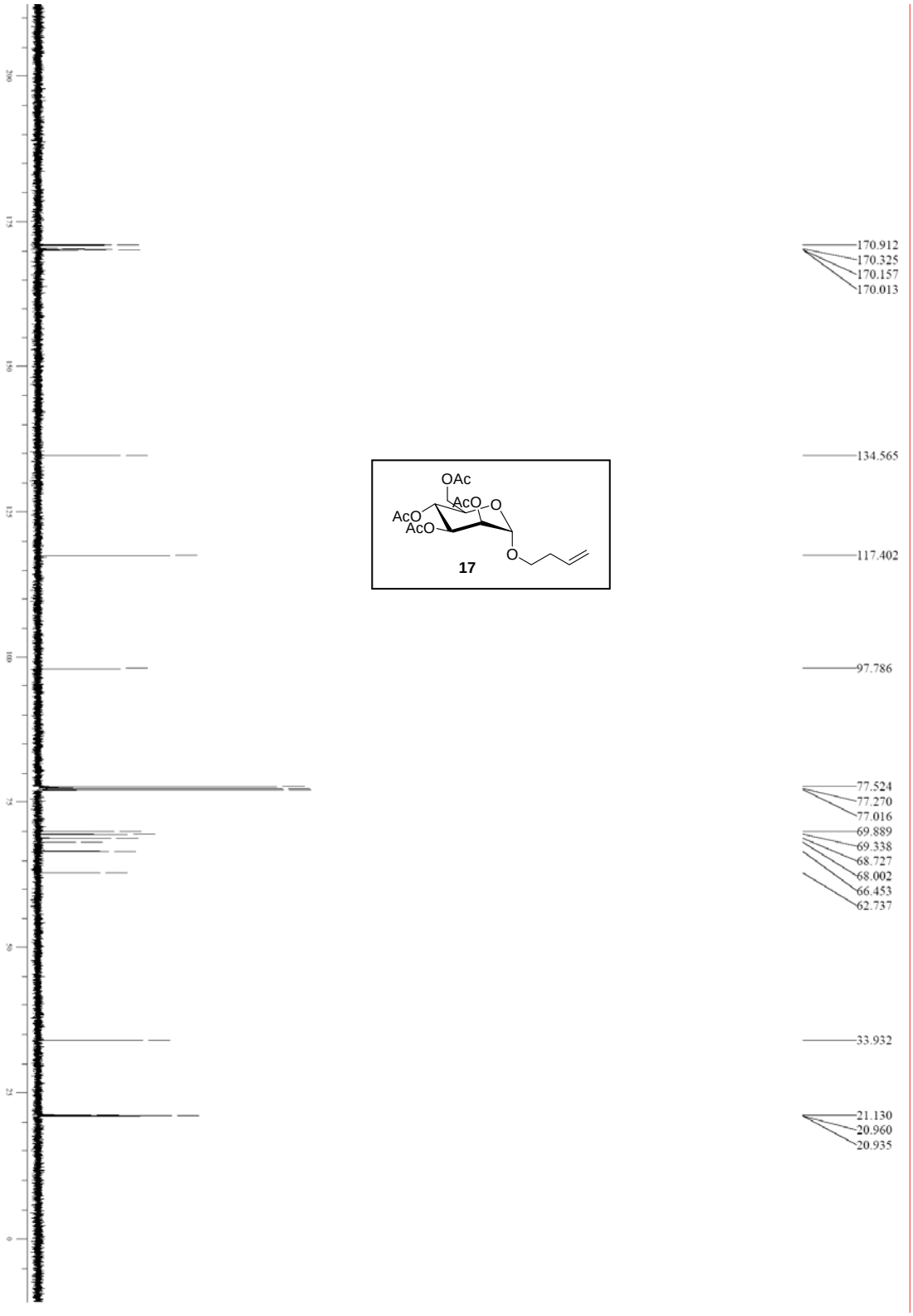


Figure S2. ^{13}C NMR spectrum of compound **17**.

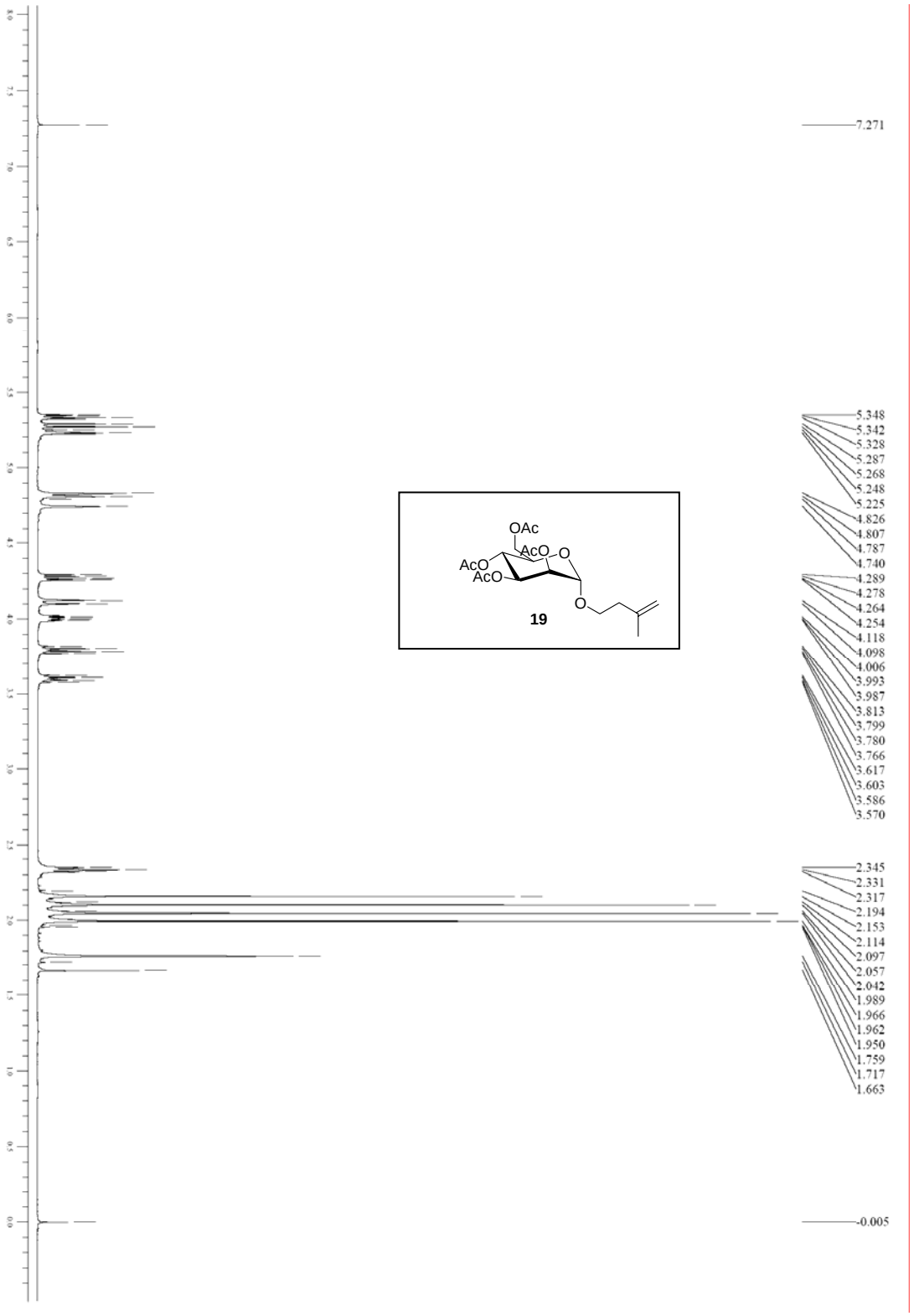


Figure S3. ^{1}H NMR spectrum of compound **19**.

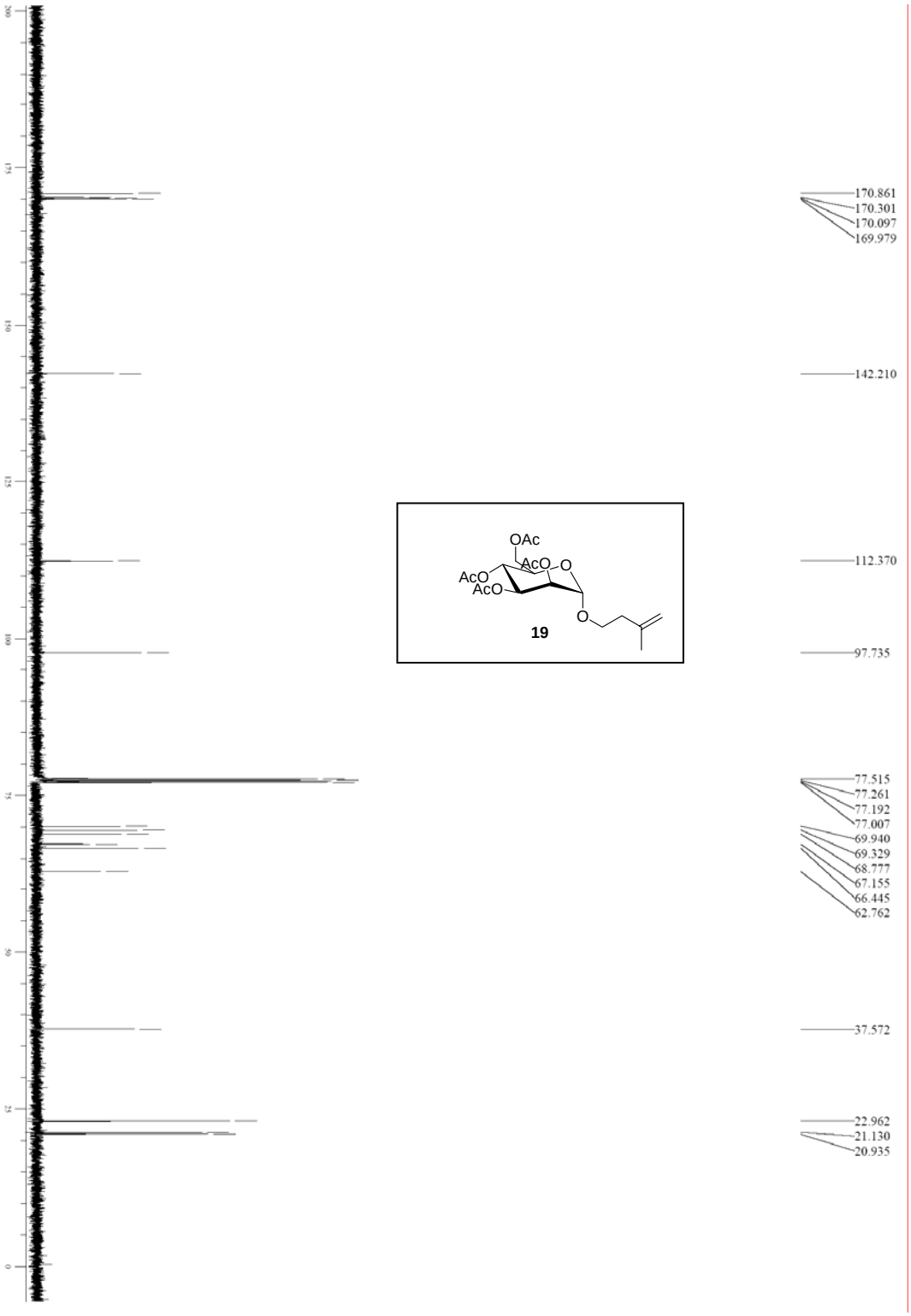


Figure S4. ^{13}C NMR spectrum of compound **19**.

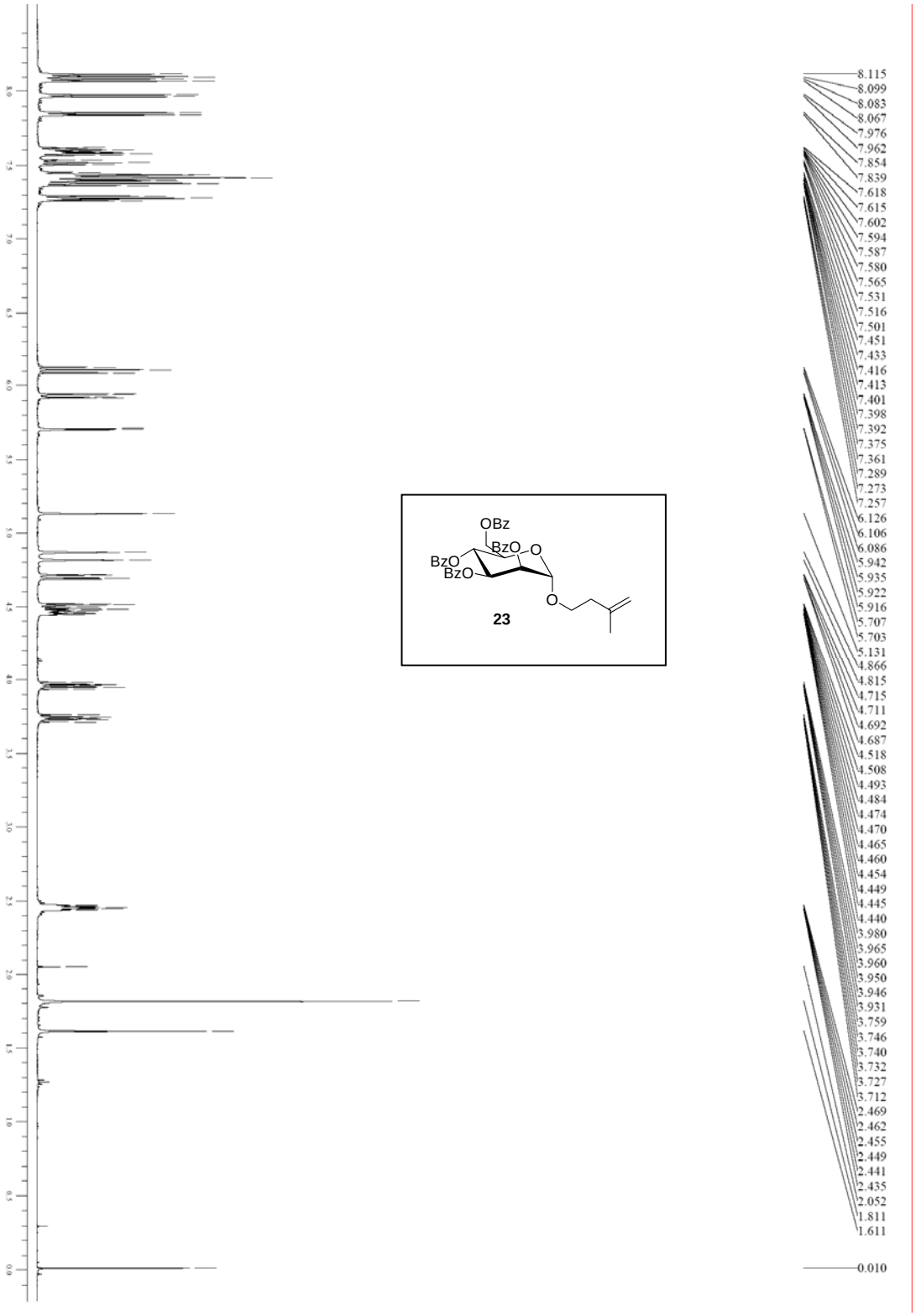


Figure S5. ^{1}H NMR spectrum of compound **23**.

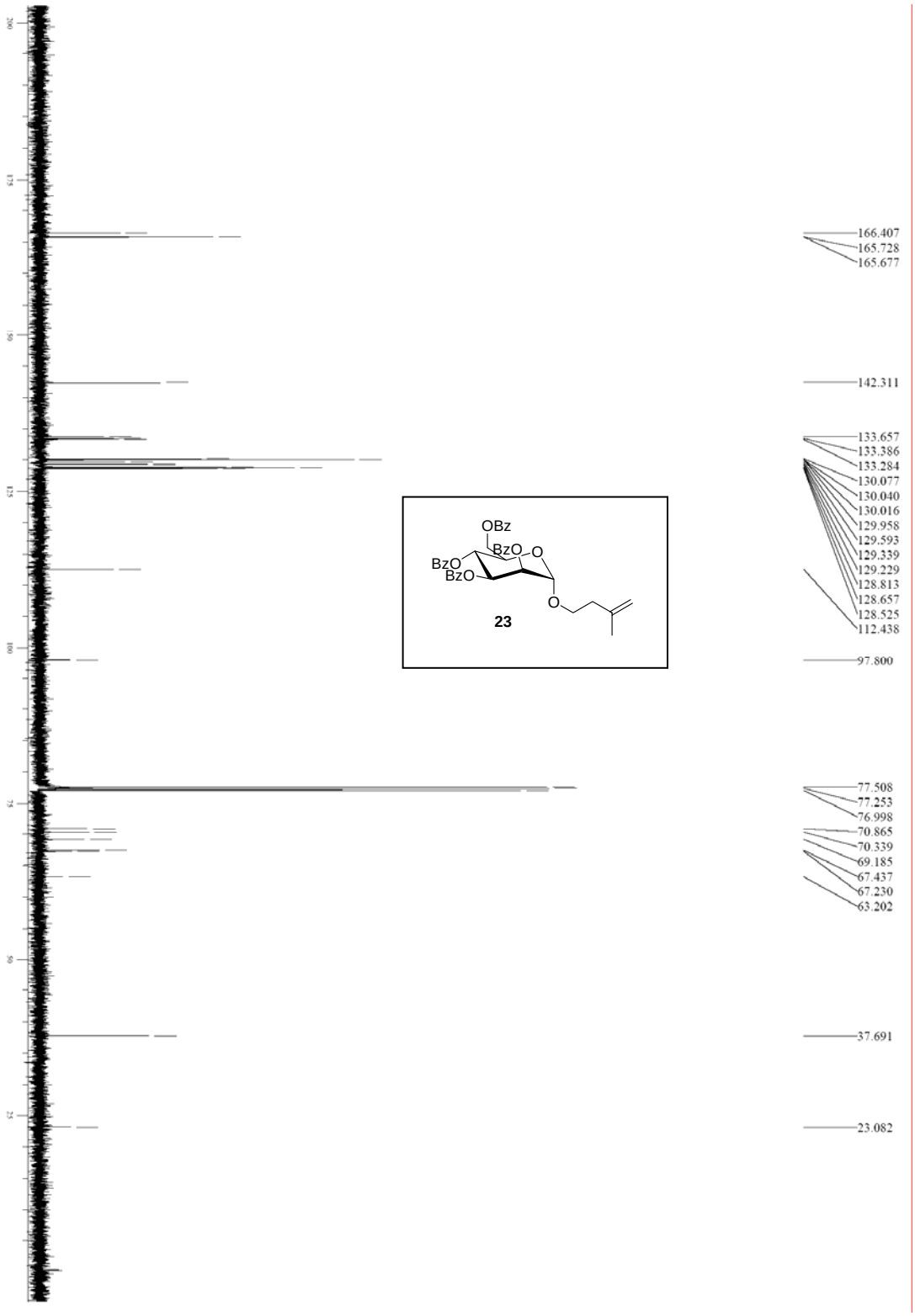


Figure S6. ^{13}C NMR spectrum of compound **23**.

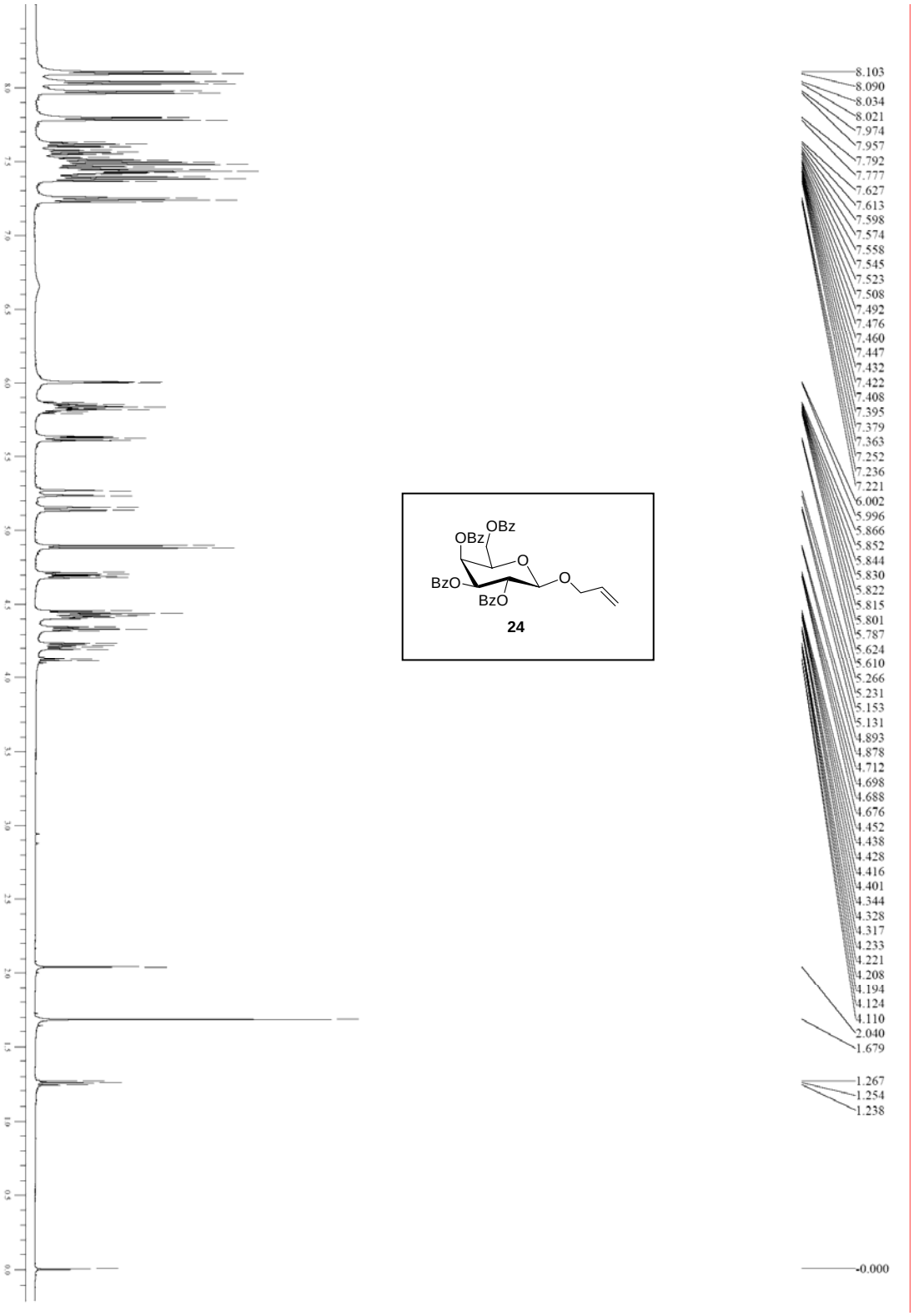


Figure S7. ^{1}H NMR spectrum of compound **24**.

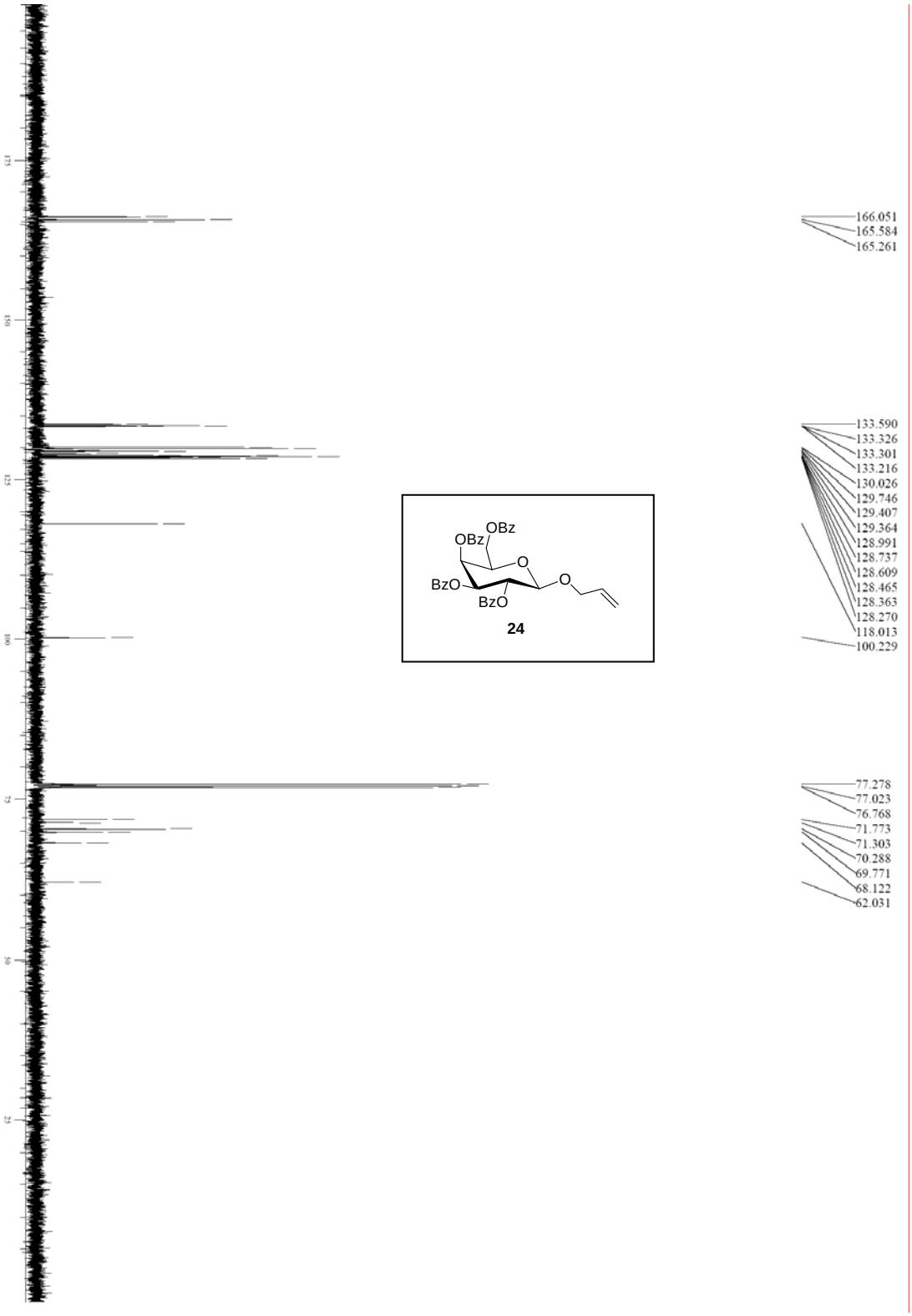


Figure S8. ^{13}C NMR spectrum of compound **24**.

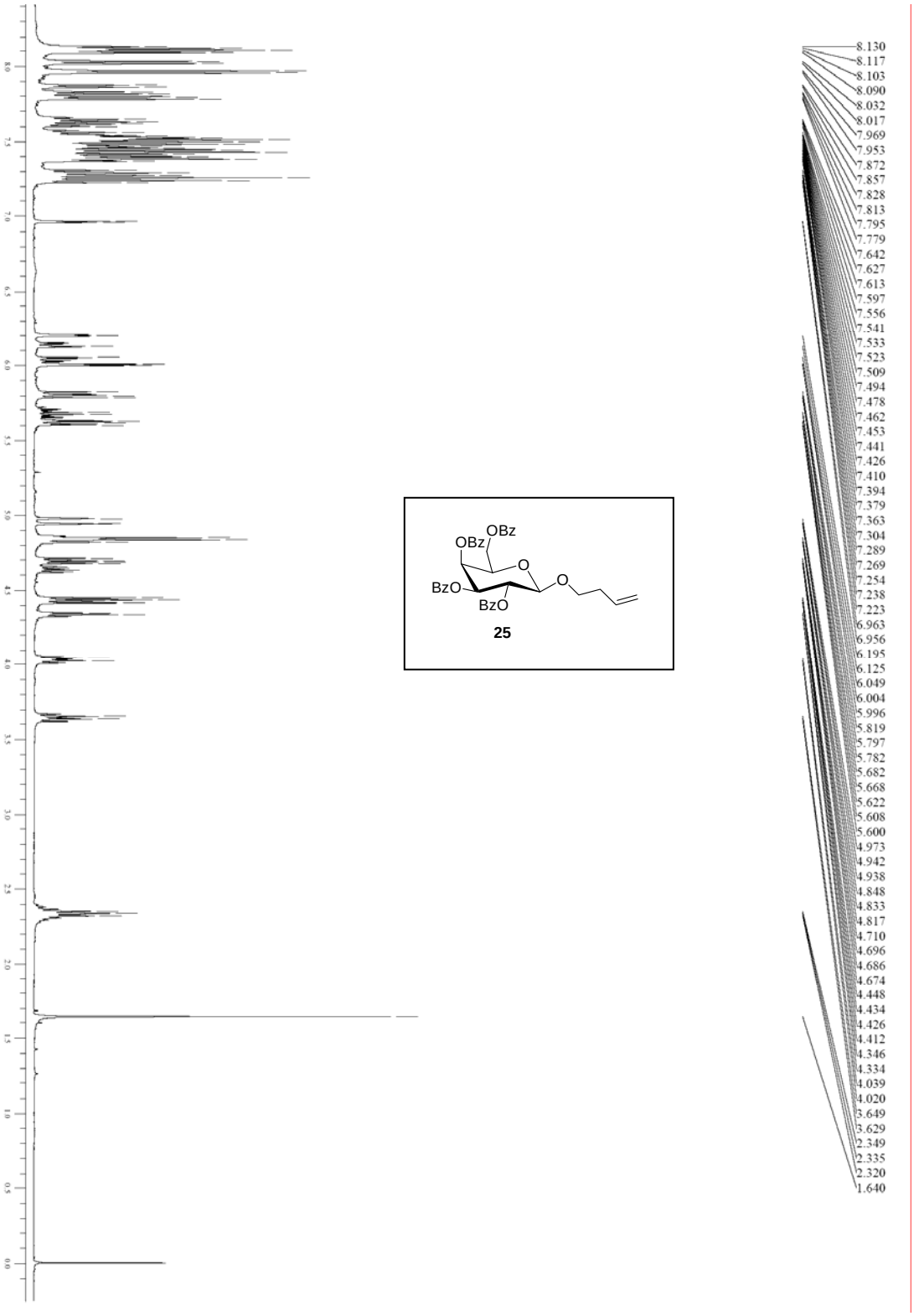


Figure S9. ^{1}H NMR spectrum of compound **25**.

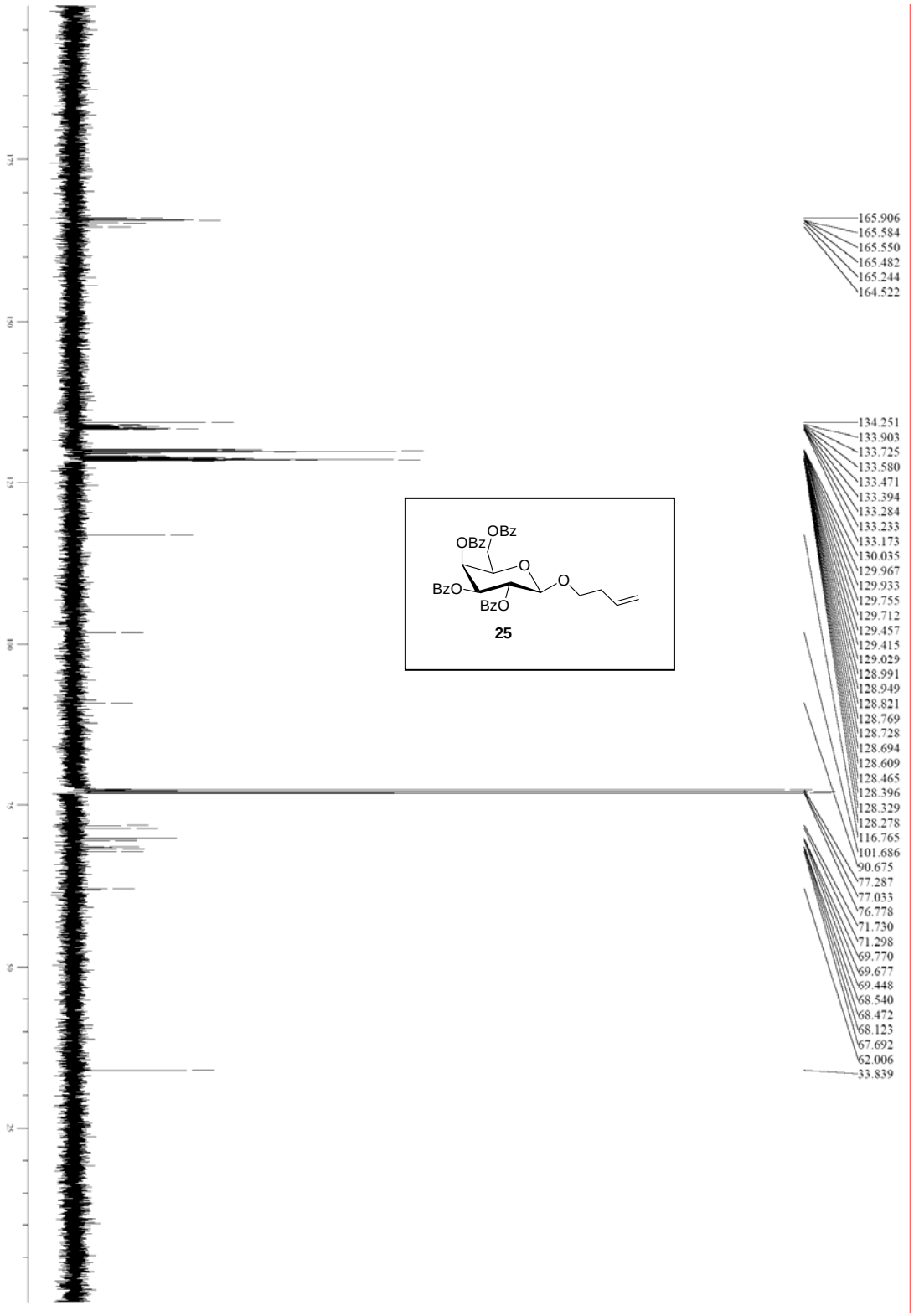


Figure S10. ^{13}C NMR spectrum of compound **25**.

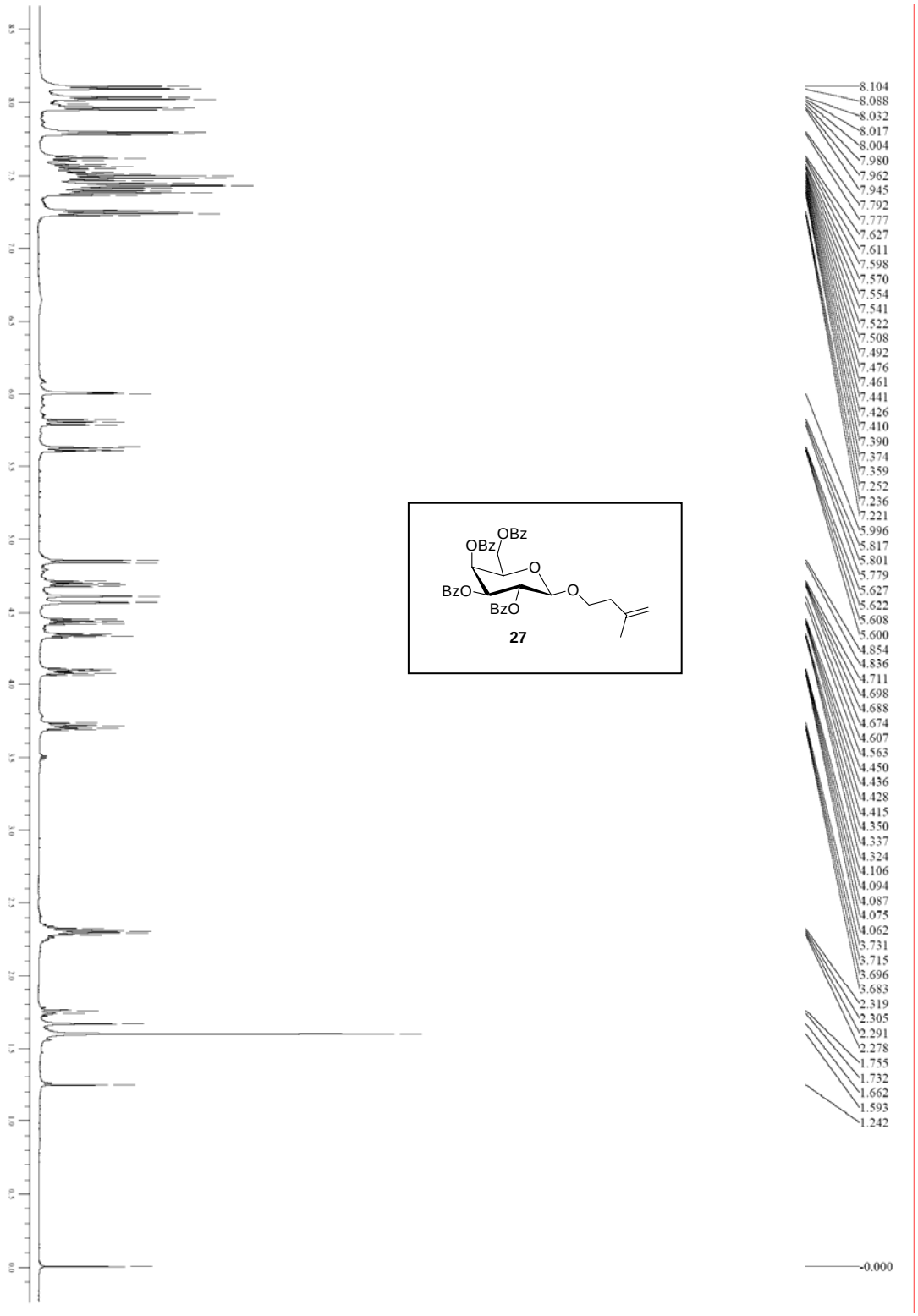


Figure S11. ^{1}H NMR spectrum of compound **27**.

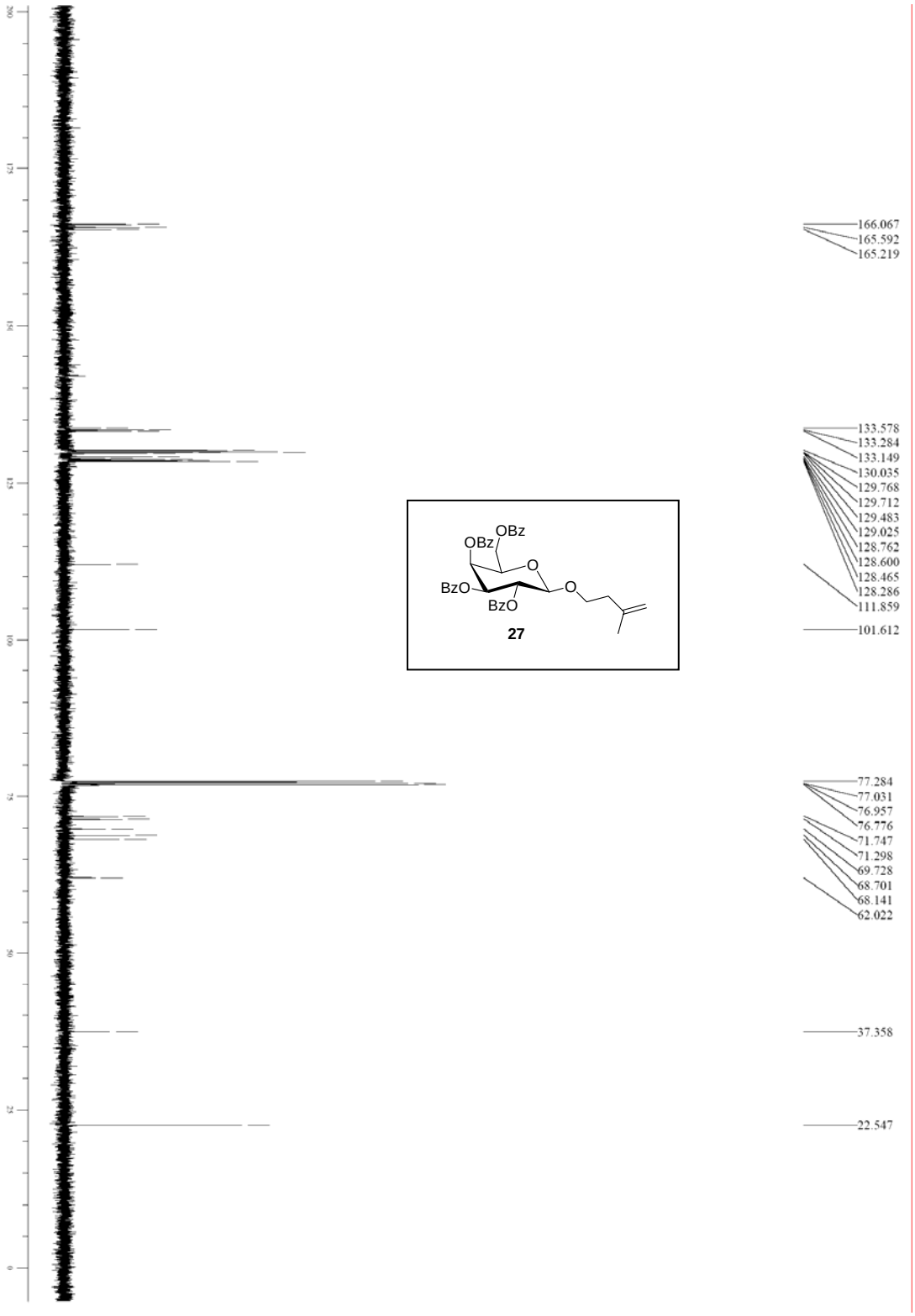


Figure S12. ^{13}C NMR spectrum of compound **27**.

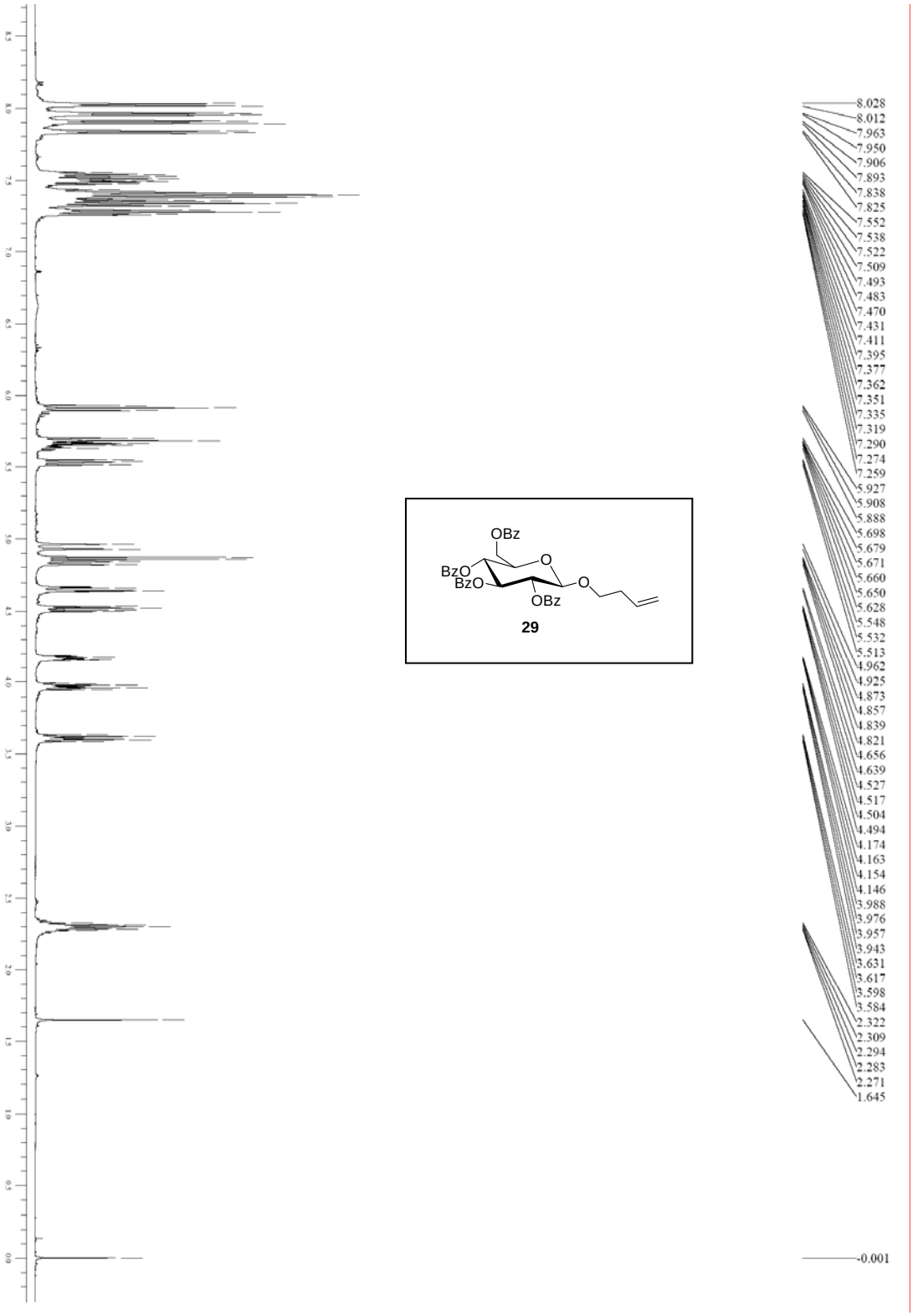


Figure S13. ^{1}H NMR spectrum of compound **29**.

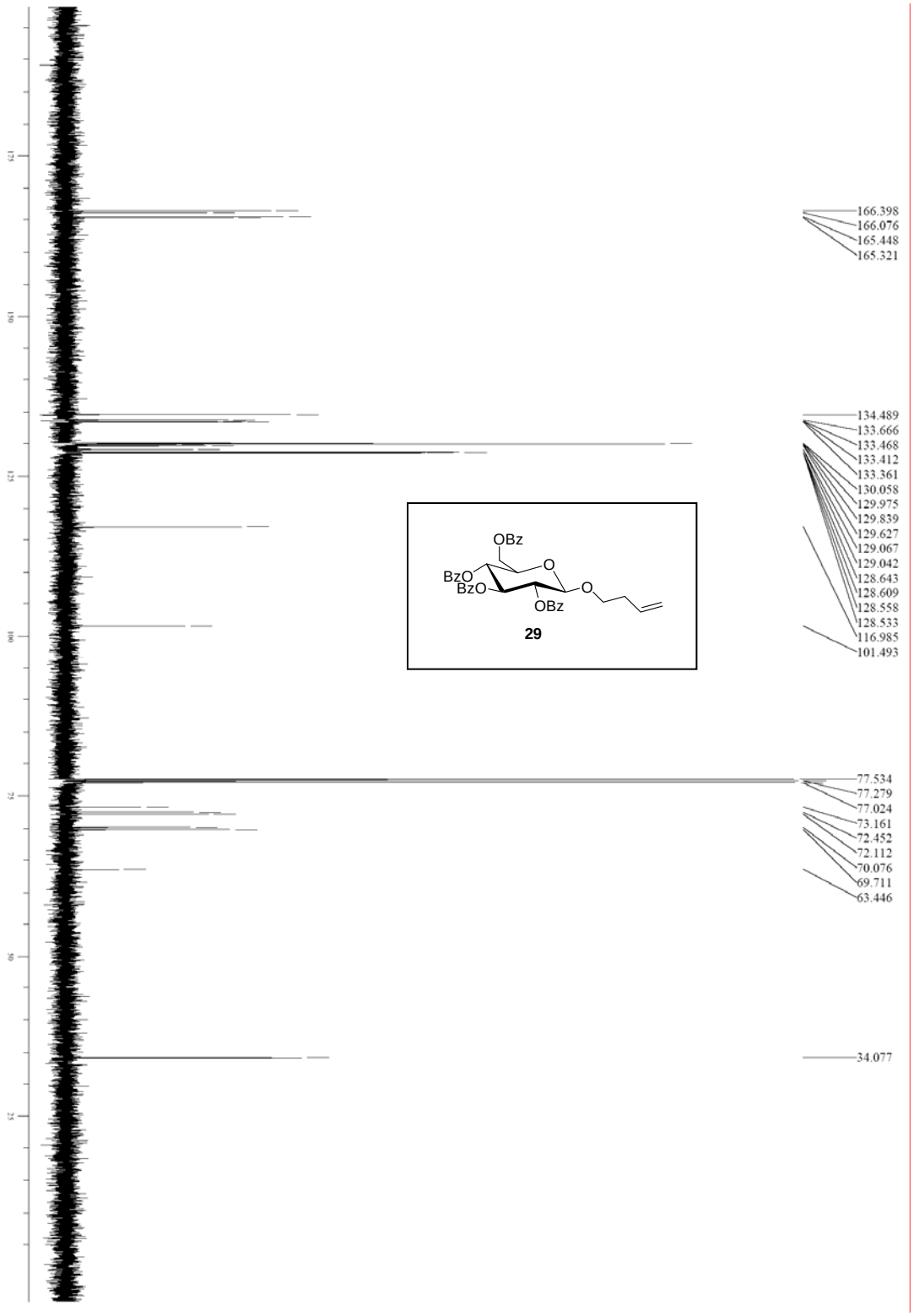
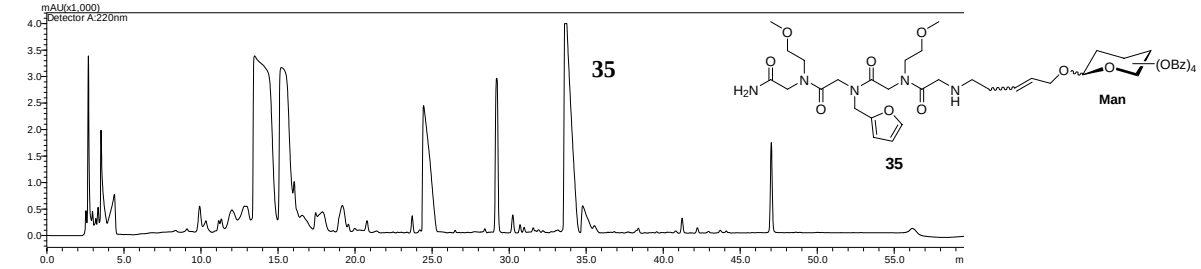


Figure S14. ^{13}C NMR spectrum of compound **29**.

HPLC chromatograms and MALDI-TOF spectra

(a)



(b)

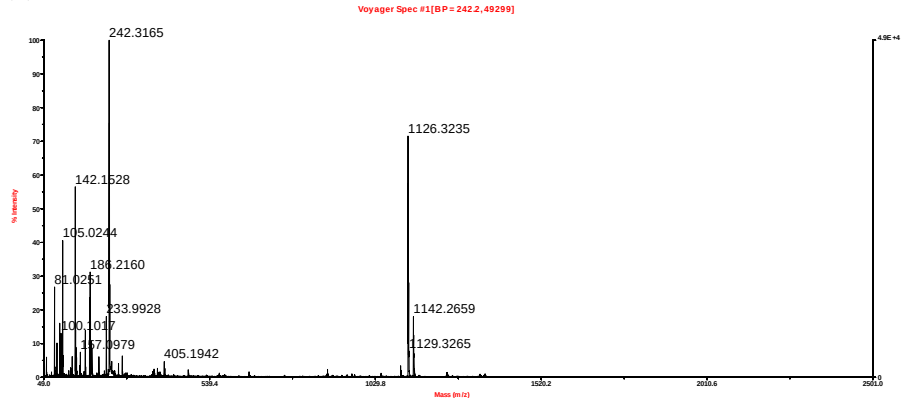
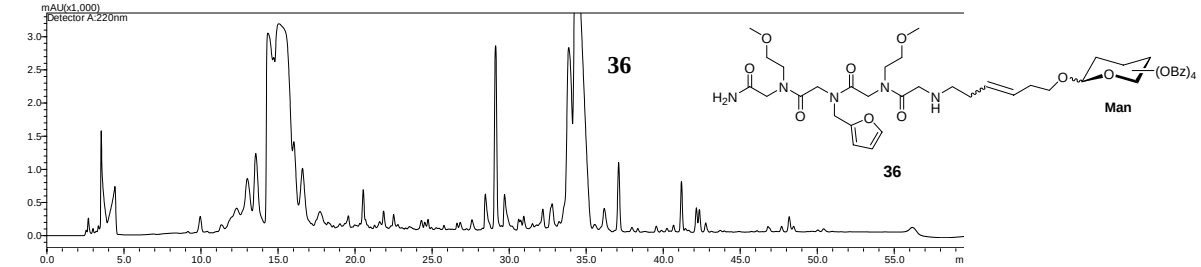


Figure S15. (a) HPLC chromatogram and (b) MALDI-TOF spectrum of compound **35**.

(a)



(b)

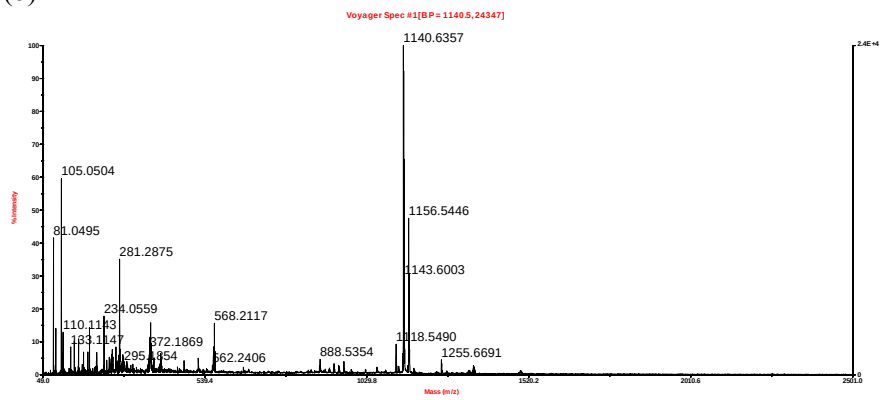
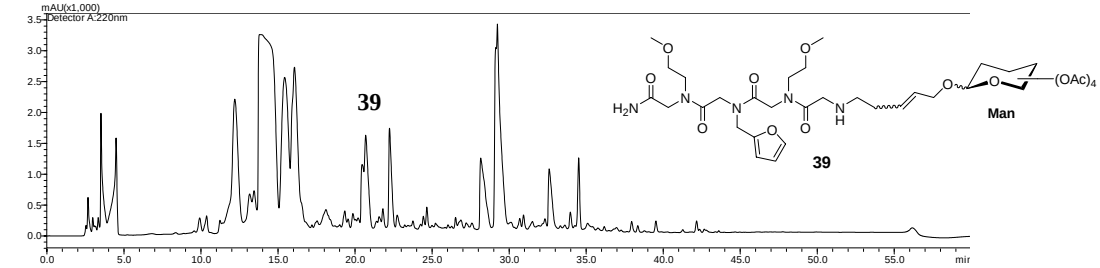


Figure S16. (a) HPLC chromatogram and (b) MALDI-TOF spectrum of compound **36**.

(a)



(b)

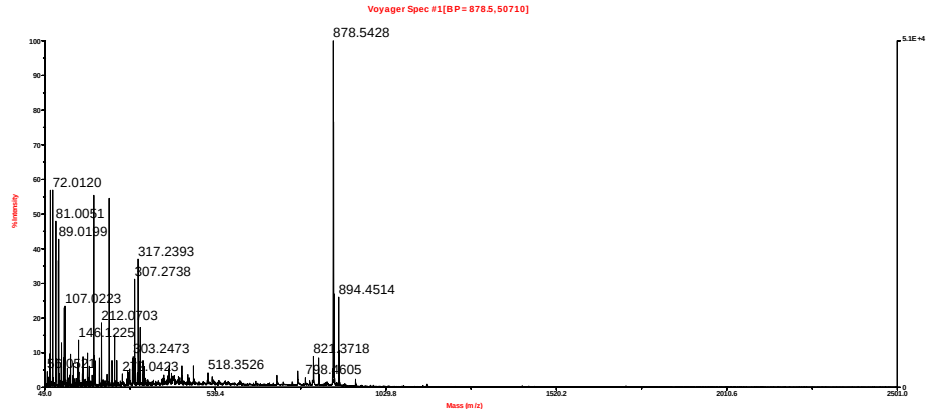
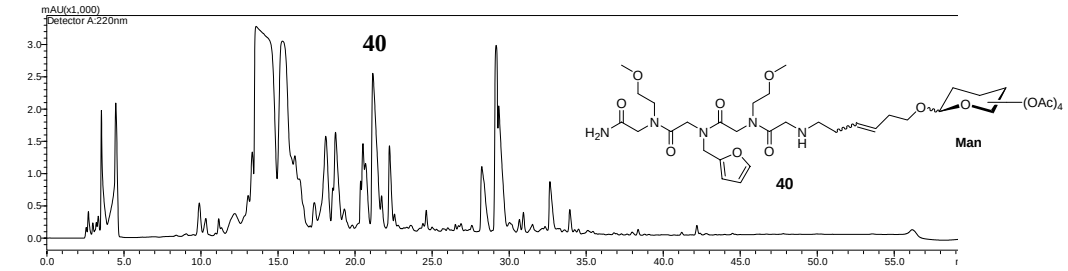


Figure S17. (a) HPLC chromatogram and (b) MALDI-TOF spectrum of compound **39**.

(a)



(b)

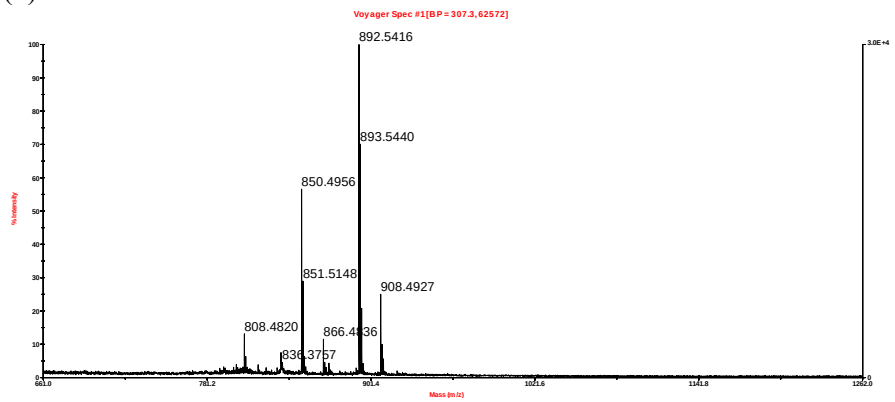
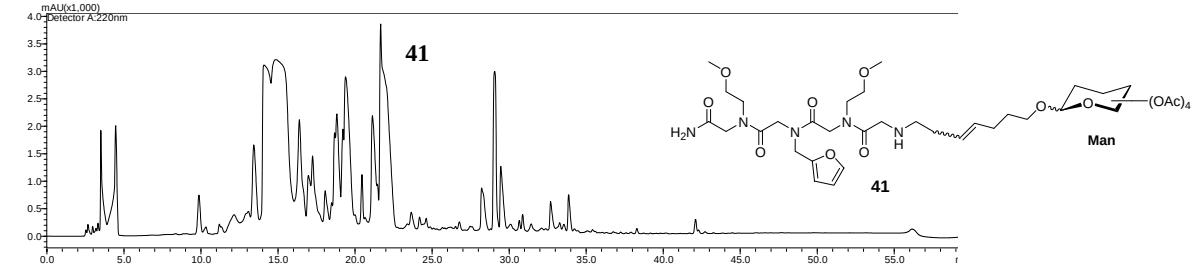


Figure S18. (a) HPLC chromatogram and (b) MALDI-TOF spectrum of compound **40**.

(a)



(b)

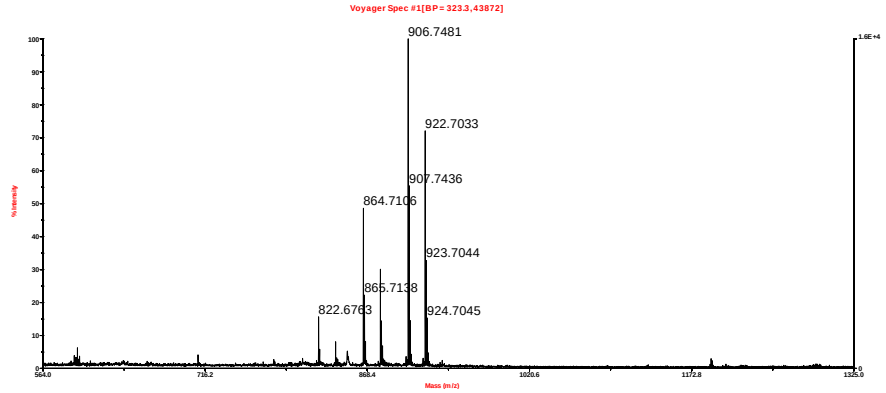
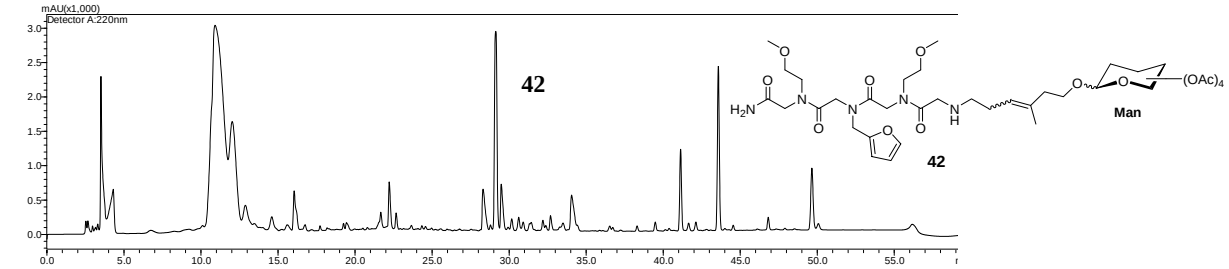


Figure S19. (a) HPLC chromatogram and (b) MALDI-TOF spectrum of compound **41**.

(a)



(b)

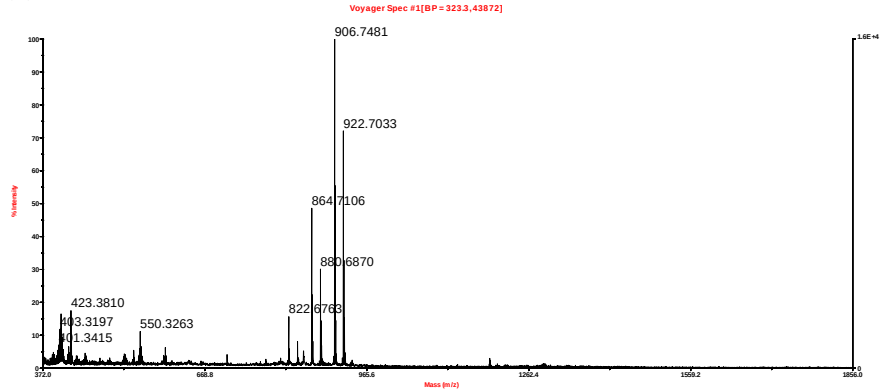
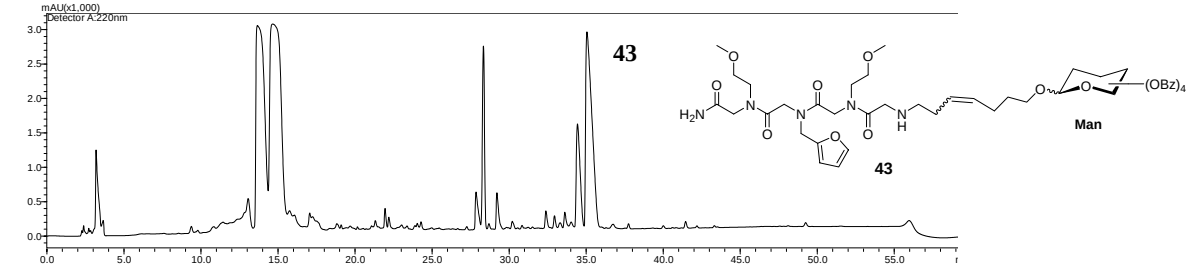


Figure S20. (a) HPLC chromatogram and (b) MALDI-TOF spectrum of compound **42**.

(a)



(b)

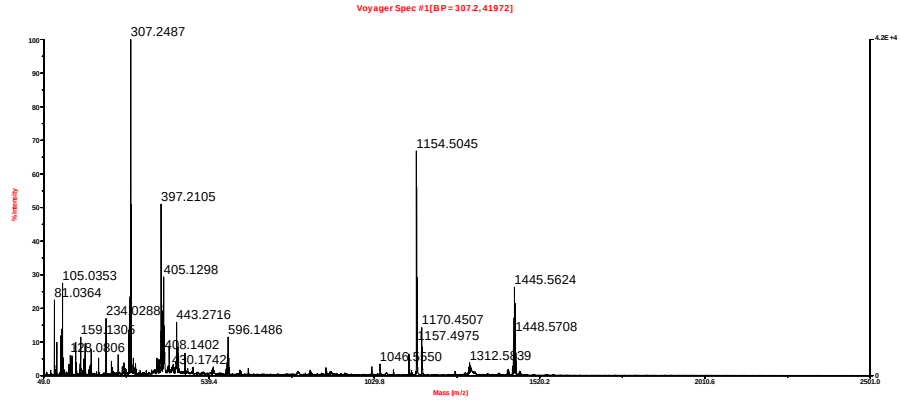
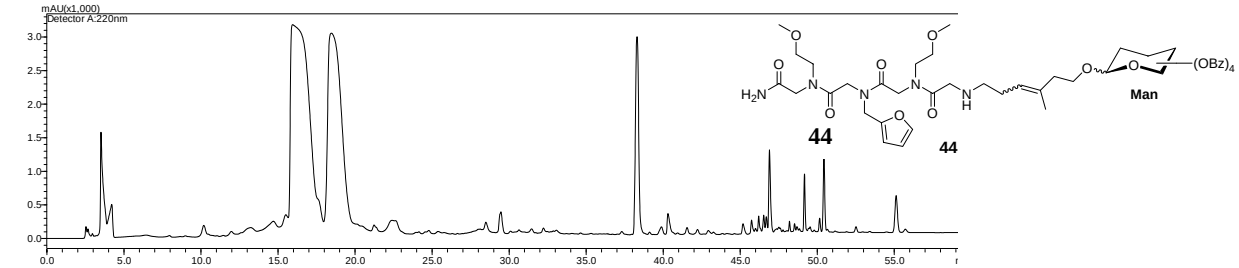


Figure S21. (a) HPLC chromatogram and (b) MALDI-TOF spectrum of compound **43**.

(a)



(b)

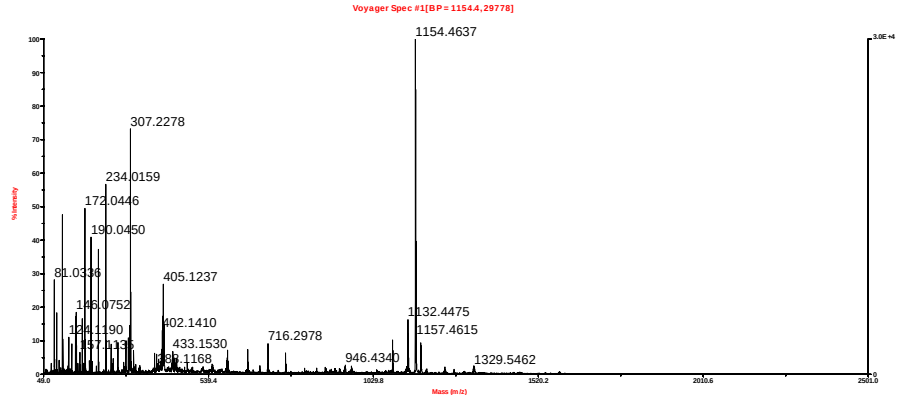
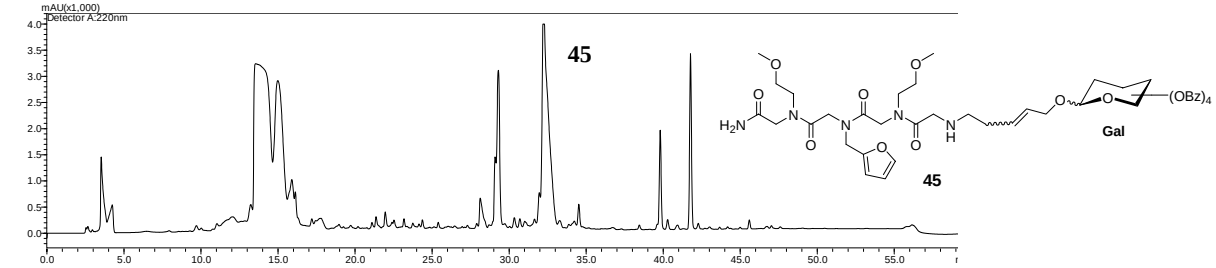


Figure S22. (a) HPLC chromatogram and (b) MALDI-TOF spectrum of compound **44**.

(a)



(b)

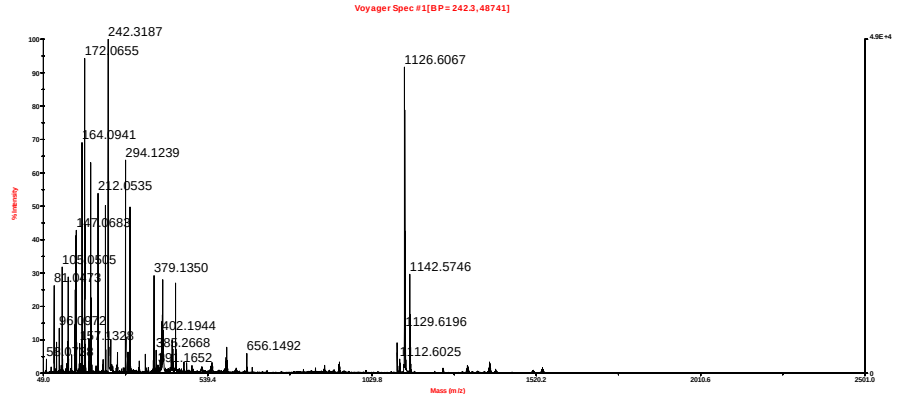
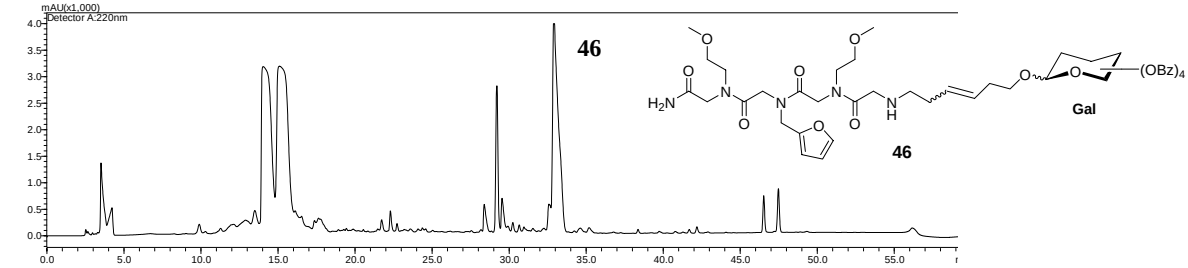


Figure S23. (a) HPLC chromatogram and (b) MALDI-TOF spectrum of compound **45**.

(a)



(b)

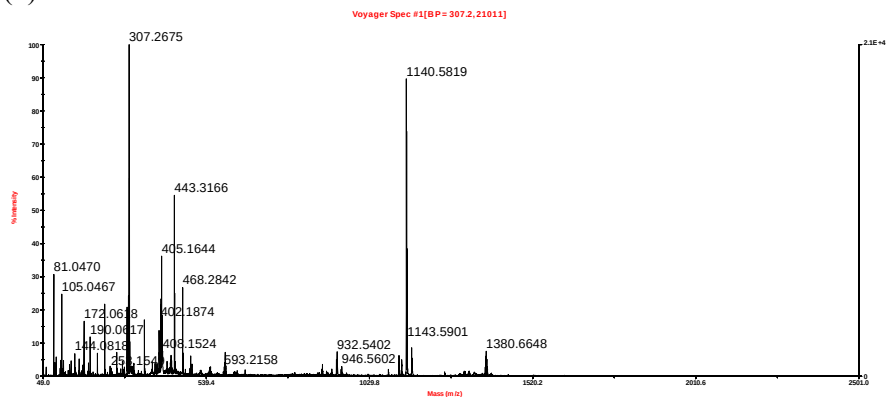


Figure S24. (a) HPLC chromatogram and (b) MALDI-TOF spectrum of compound **46**.

(a)

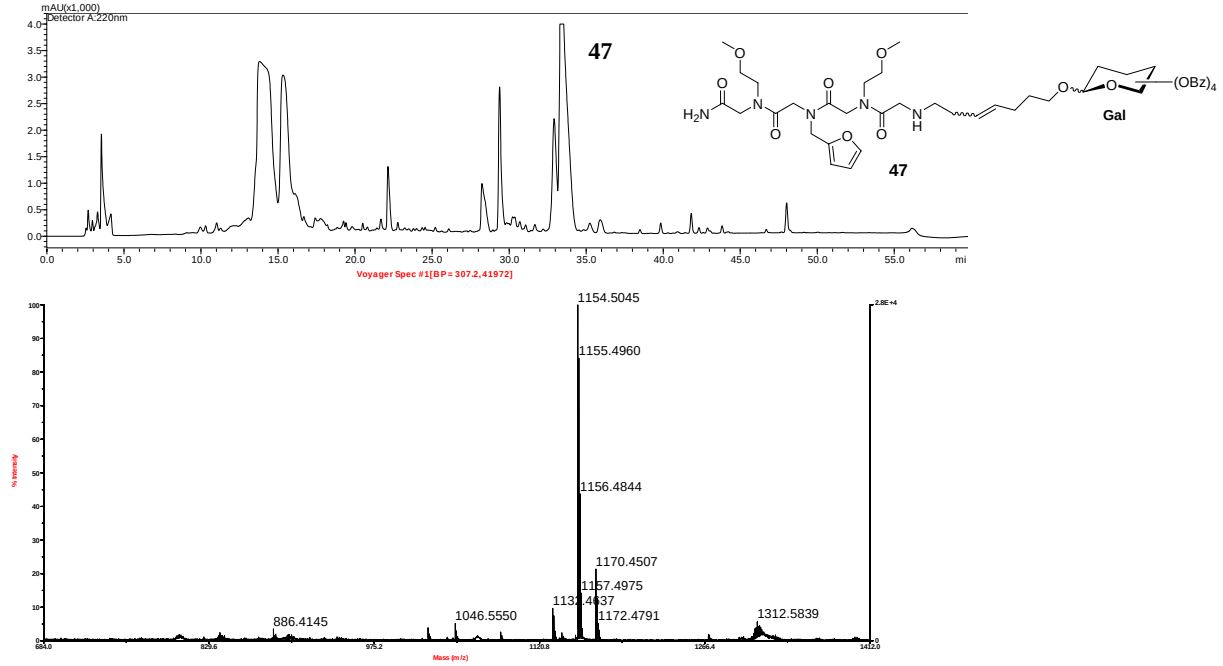
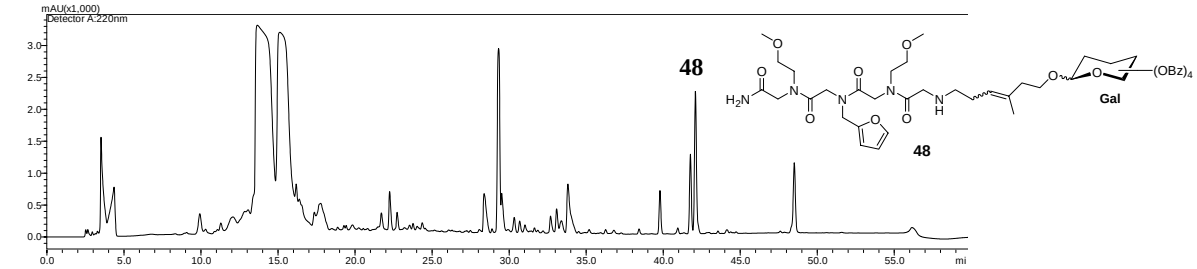


Figure S25. (a) HPLC chromatogram and (b) MALDI-TOF spectrum of compound **47**.

(a)



(b)

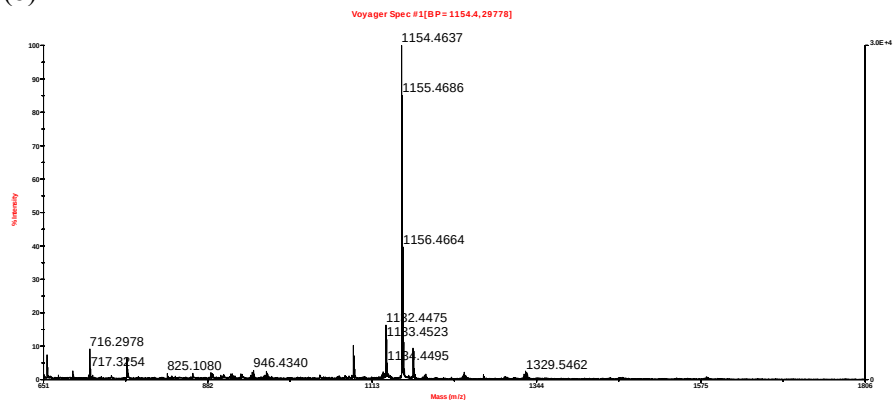
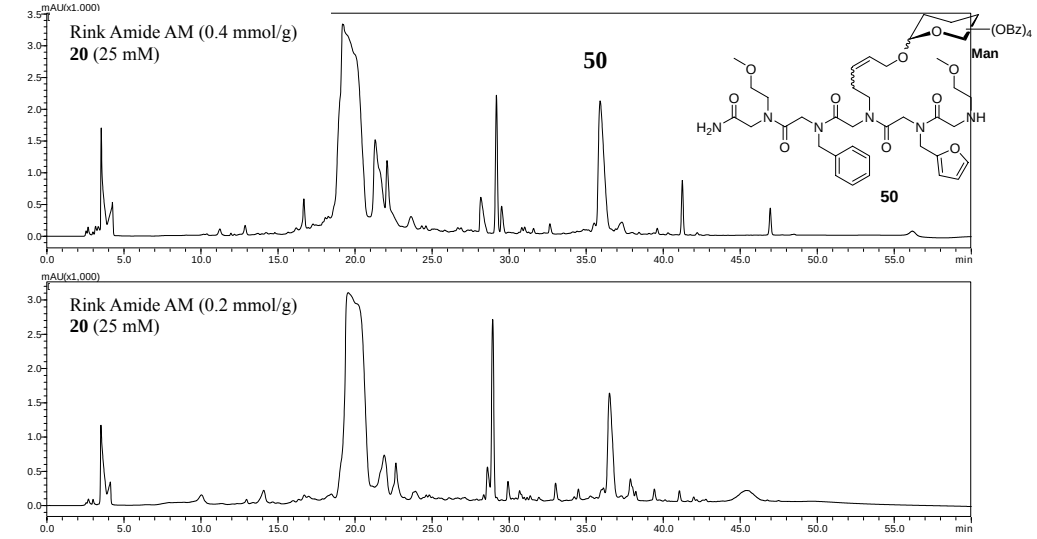


Figure S26. (a) HPLC chromatogram and (b) MALDI-TOF spectrum of compound **48**.

(a)



(b)

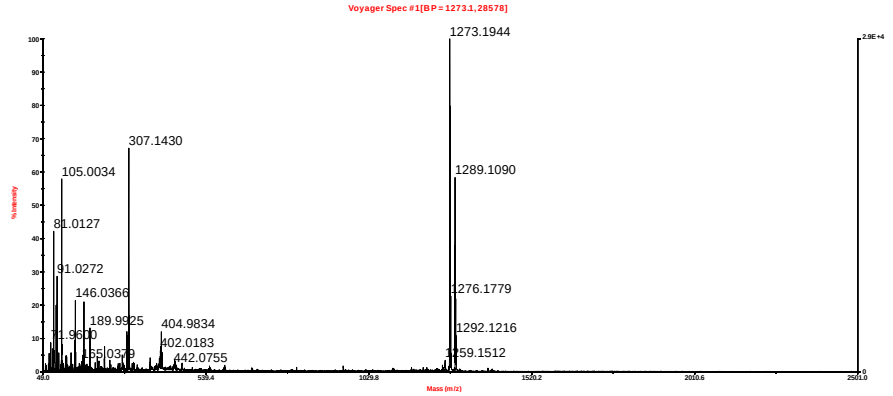
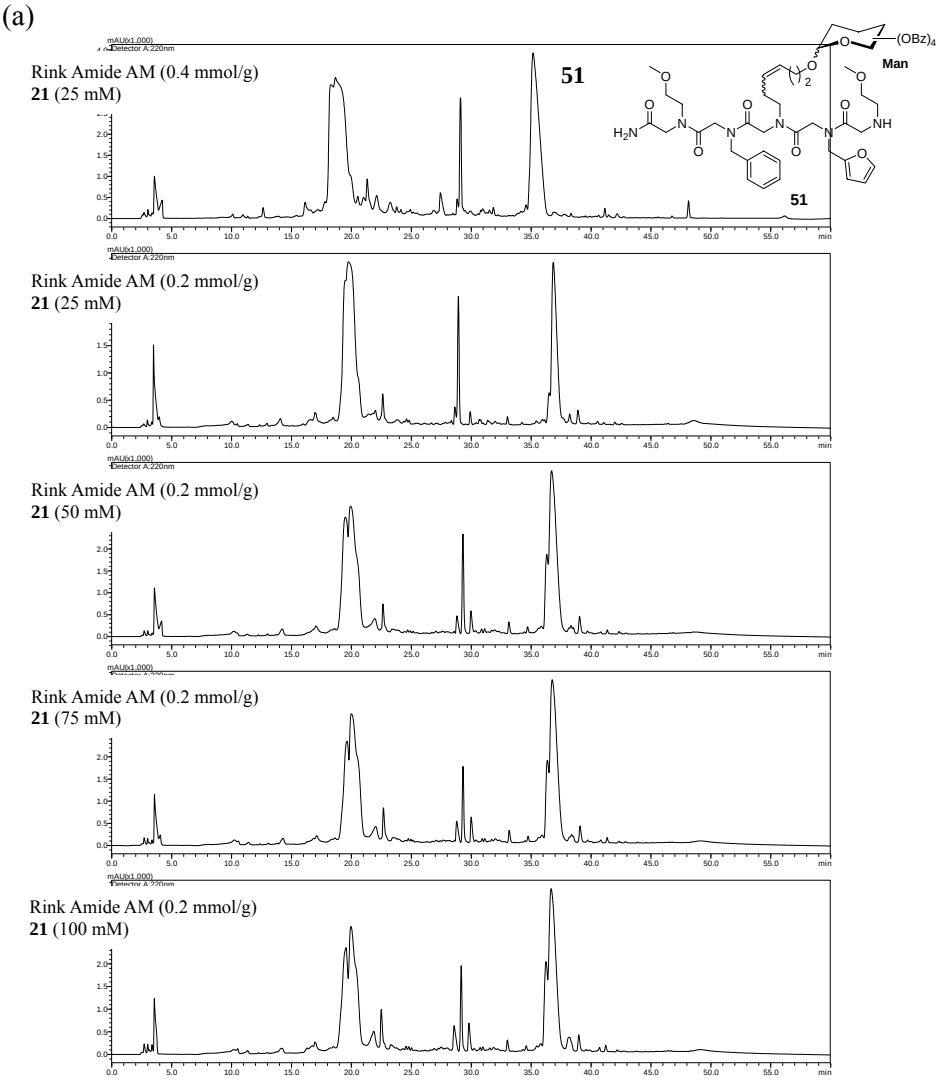


Figure S27. (a) HPLC chromatograms and (b) MALDI-TOF spectrum of compound **50**.

(a)



(b)

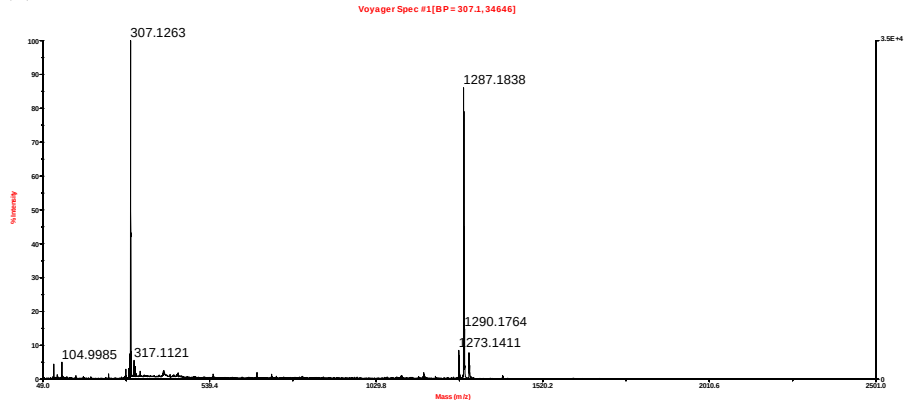
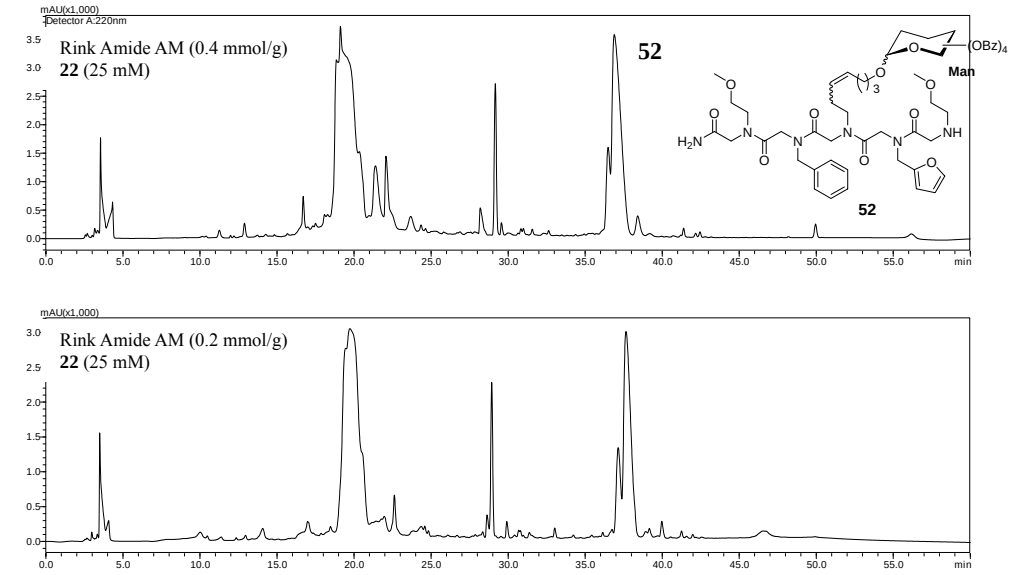


Figure S28. (a) HPLC chromatograms and (b) MALDI-TOF spectrum of compound **51**.

(a)



(b)

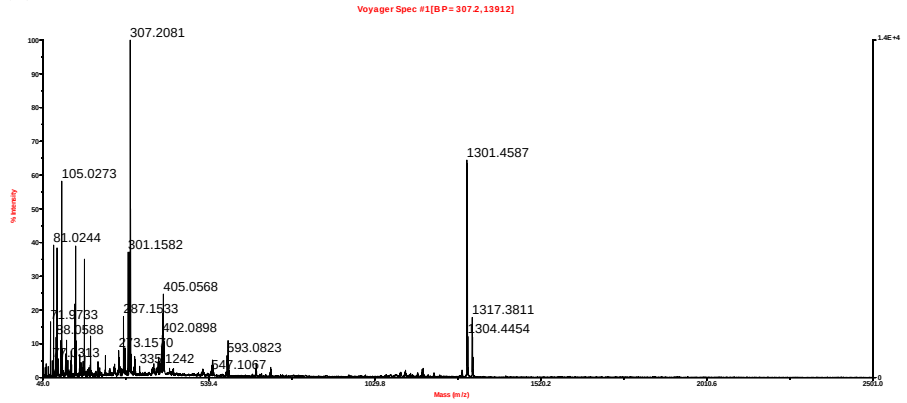
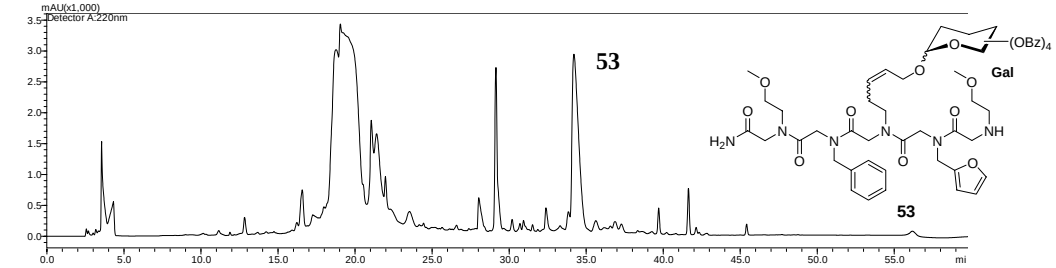


Figure S29. (a) HPLC chromatograms and (b) MALDI-TOF spectrum of compound **52**.

(a)



(b)

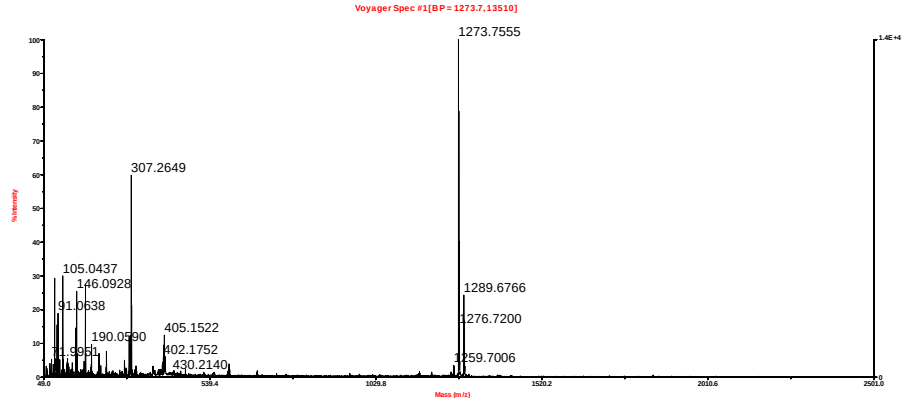
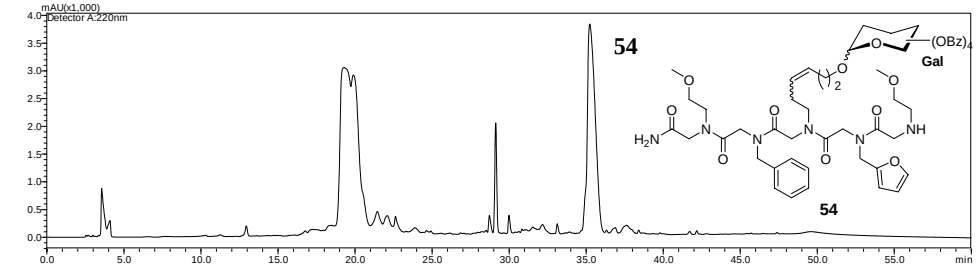


Figure S30. (a) HPLC chromatogram and (b) MALDI-TOF spectrum of compound **53**.

(a)



(b)

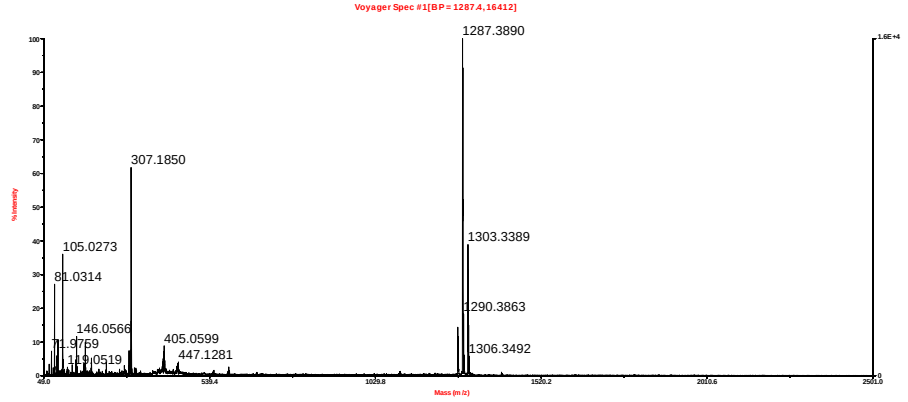
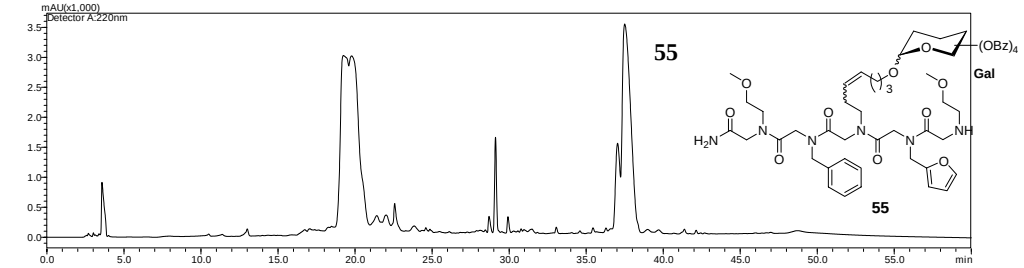


Figure S31. (a) HPLC chromatogram and (b) MALDI-TOF spectrum of compound **54**.

(a)



(b)

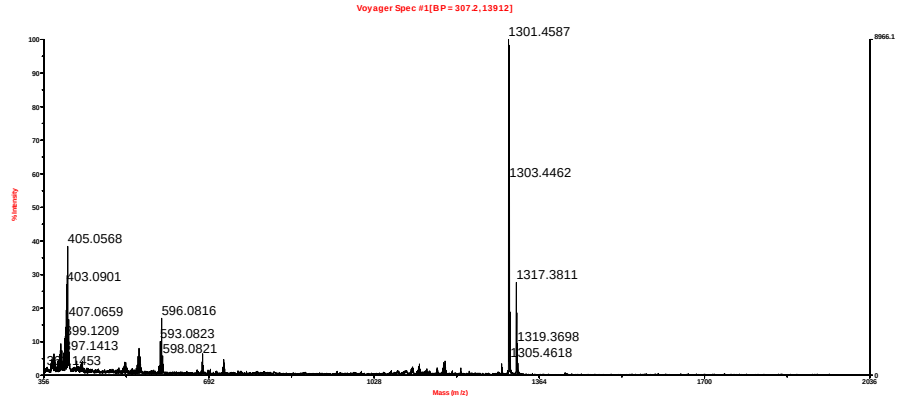
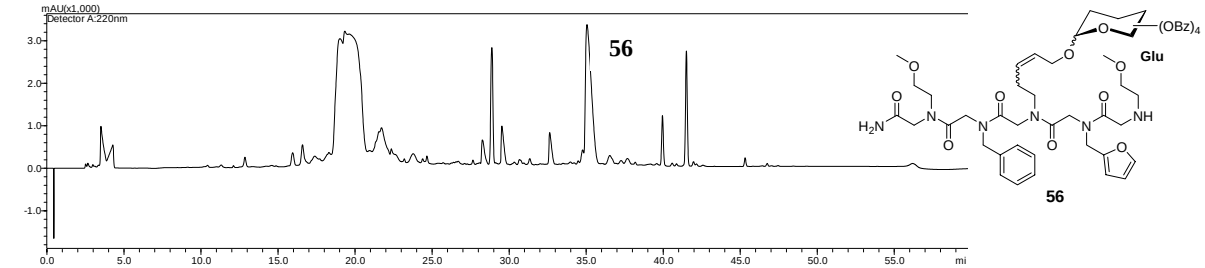


Figure S32. (a) HPLC chromatogram and (b) MALDI-TOF spectrum of compound **55**.

(a)



(b)

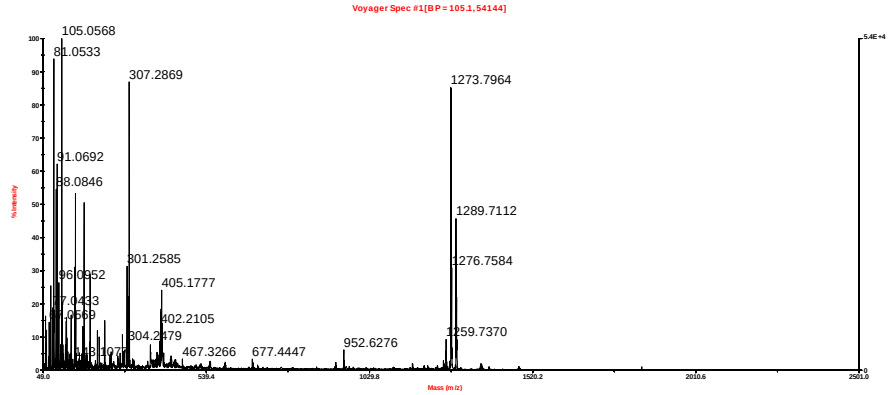
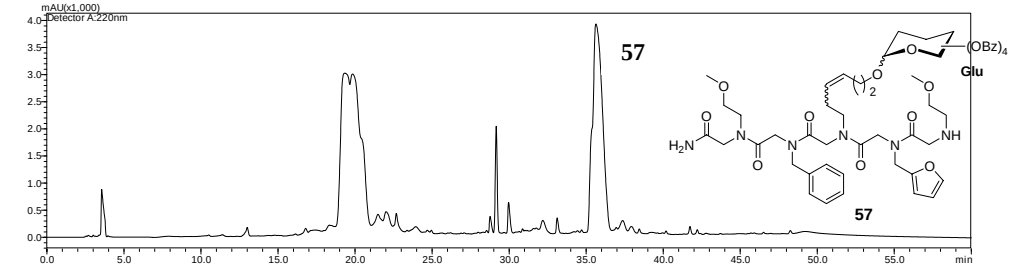


Figure S33. (a) HPLC chromatogram and (b) MALDI-TOF spectrum of compound **56**.

(a)



(b)

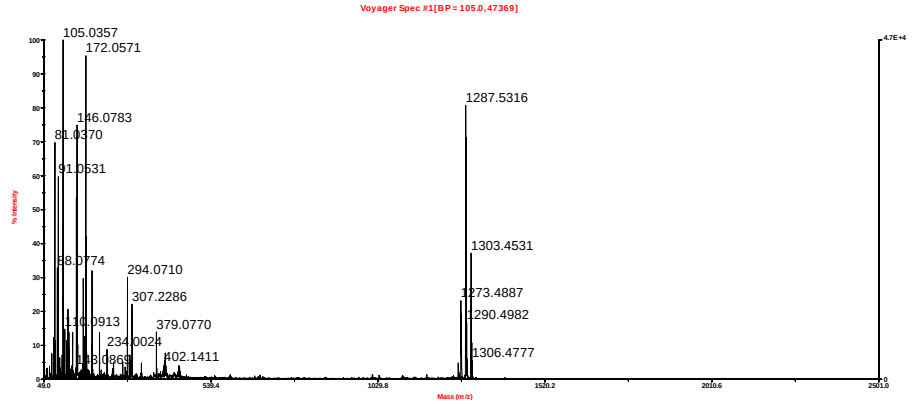
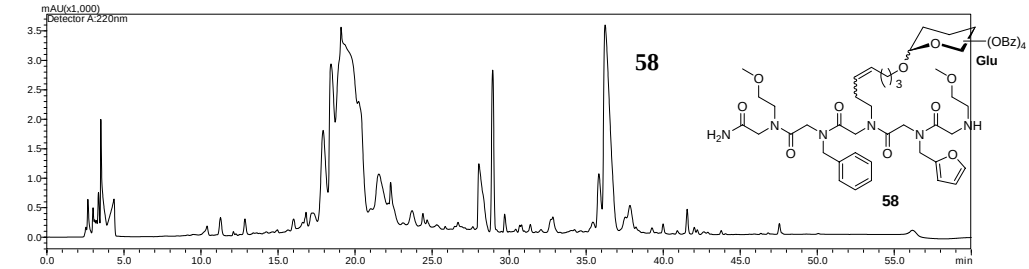


Figure S34. (a) HPLC chromatogram and (b) MALDI-TOF spectrum of compound **57**.

(a)



(b)

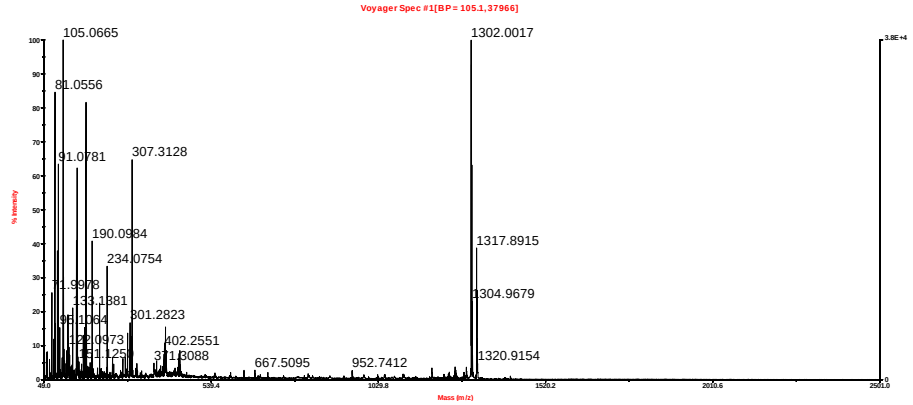
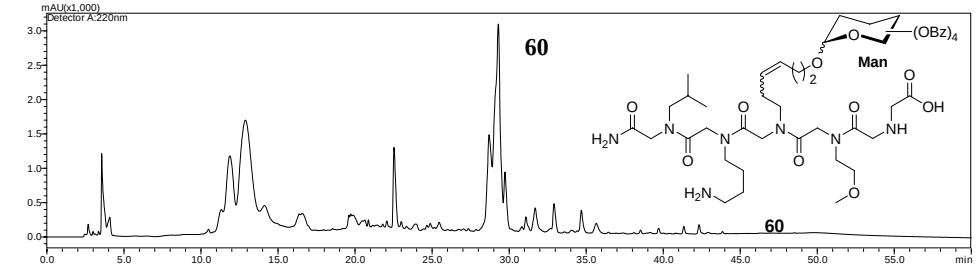


Figure S35. (a) HPLC chromatogram and (b) MALDI-TOF spectrum of compound **58**.

(a)



(b)

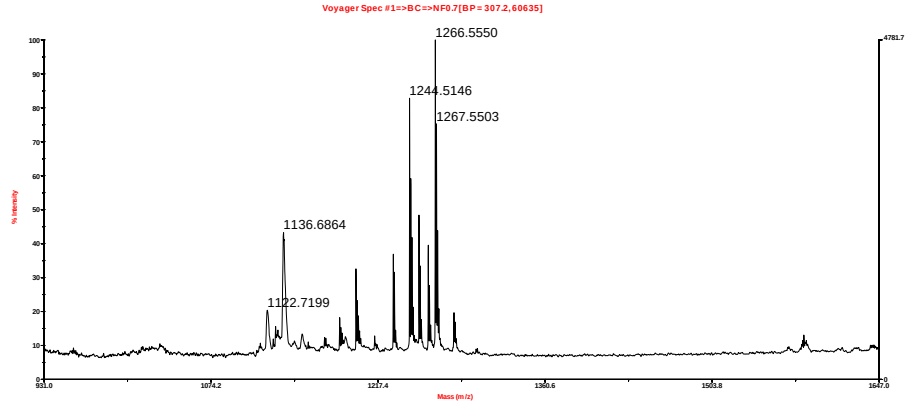
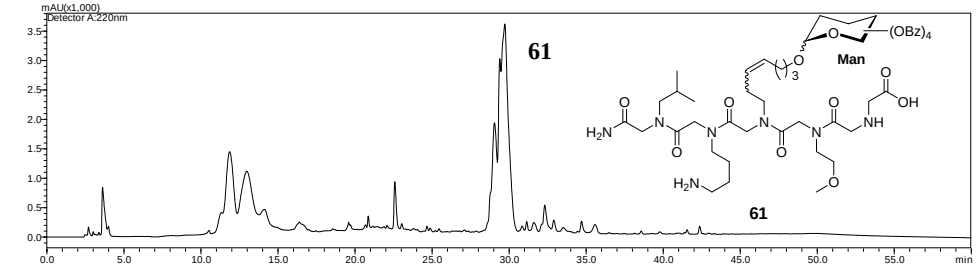


Figure S36. (a) HPLC chromatogram and (b) MALDI-TOF spectrum of compound **60**.

(a)



(b)

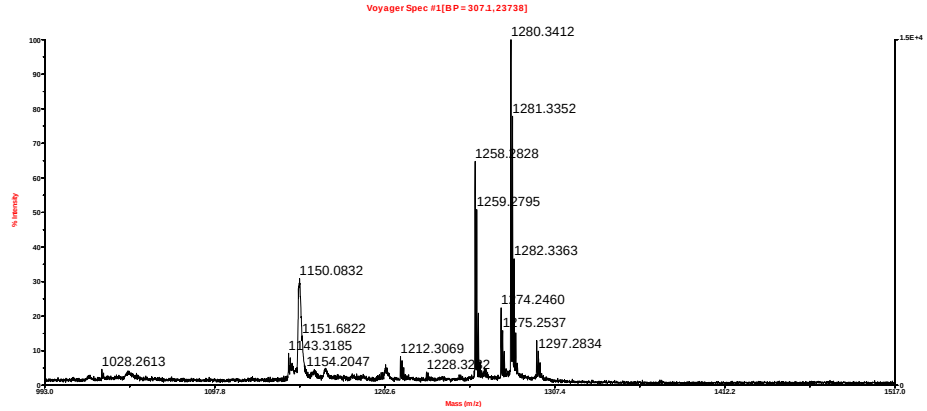
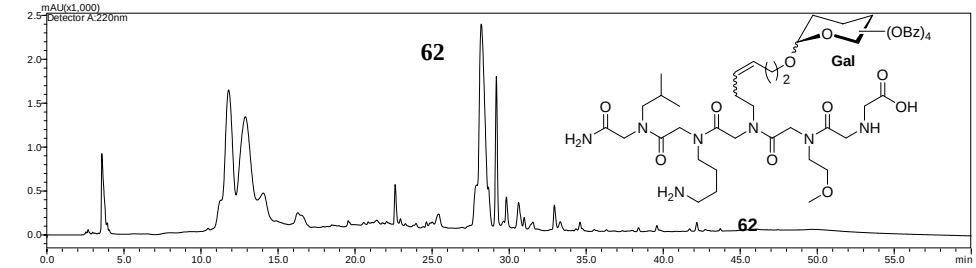


Figure S37. (a) HPLC chromatogram and (b) MALDI-TOF spectrum of compound **61**.

(a)



(b)

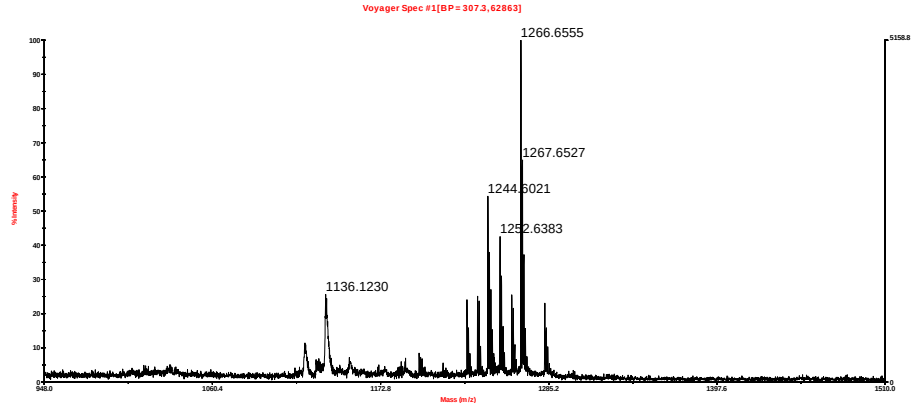
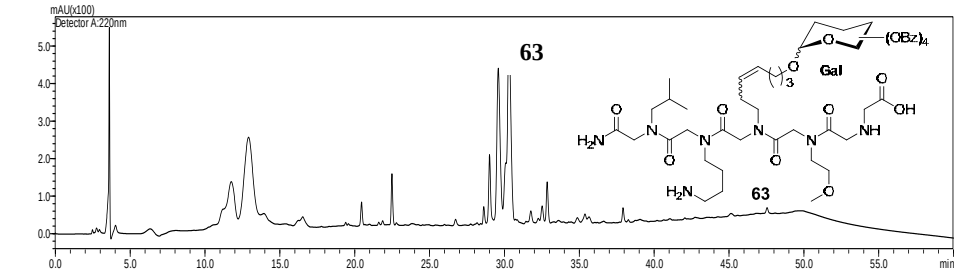


Figure S38. (a) HPLC chromatogram and (b) MALDI-TOF spectrum of compound **62**.

(a)



(b)

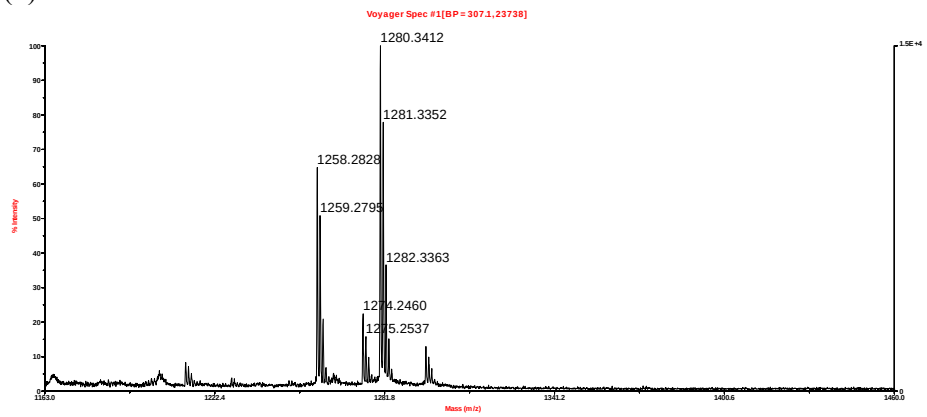
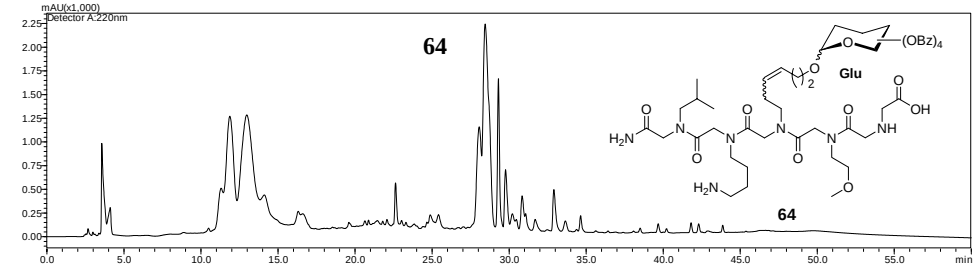


Figure S39. (a) HPLC chromatogram and (b) MALDI-TOF spectrum of compound **63**.

(a)



(b)

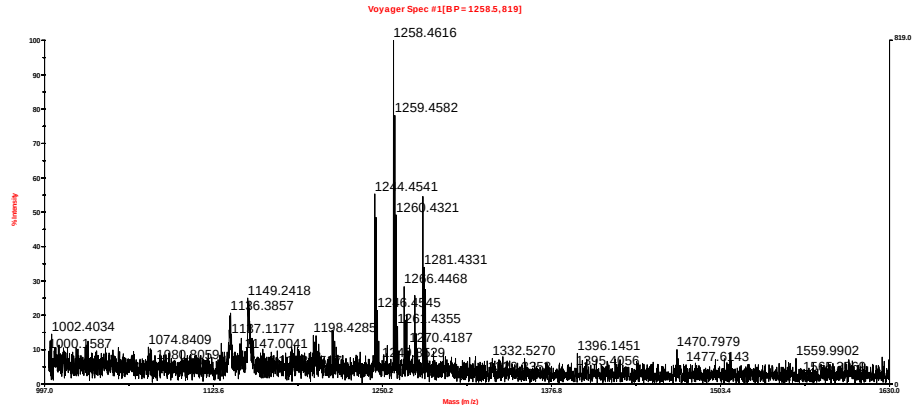
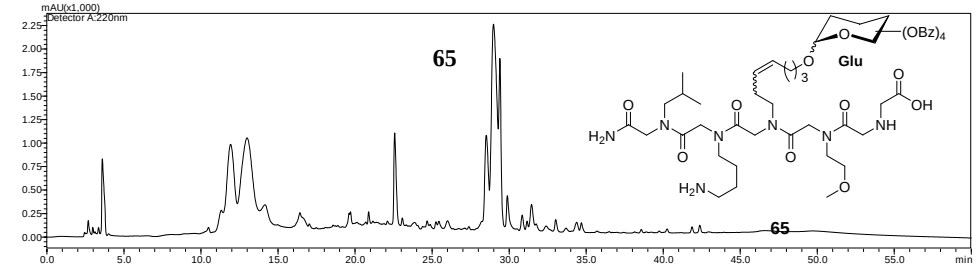


Figure S40. (a) HPLC chromatogram and (b) MALDI-TOF spectrum of compound **64**.

(a)



(b)

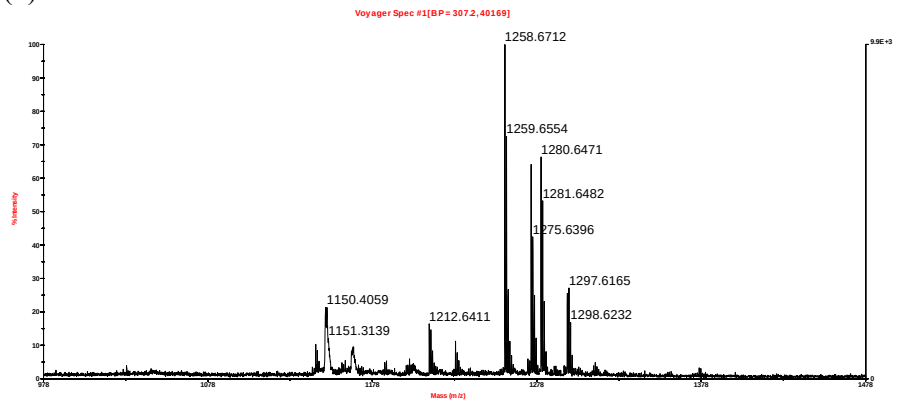
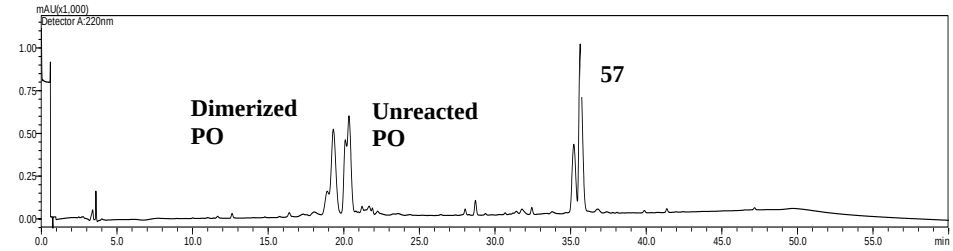


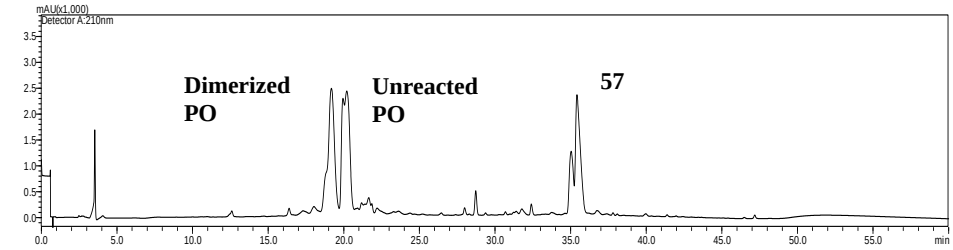
Figure S41. (a) HPLC chromatogram and (b) MALDI-TOF spectrum of compound **65**.

(a) at 220 nm



Conv.: 42%

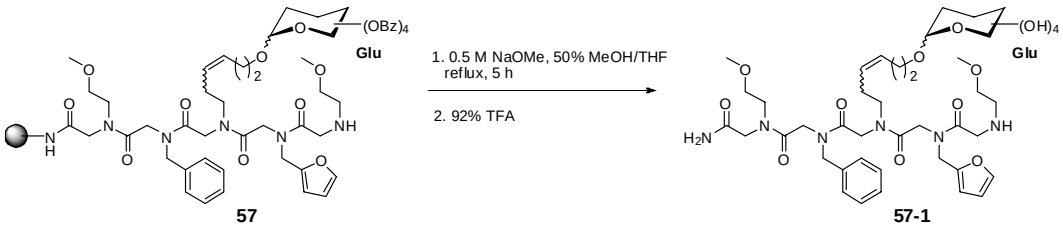
(b) at 210 nm



Conv.: 38%

Figure S42. Comparison of HPLC chromatograms of glycopeptoid (**57**)

Scheme S2. Debenzoylation of glycopeptoid (**57**)



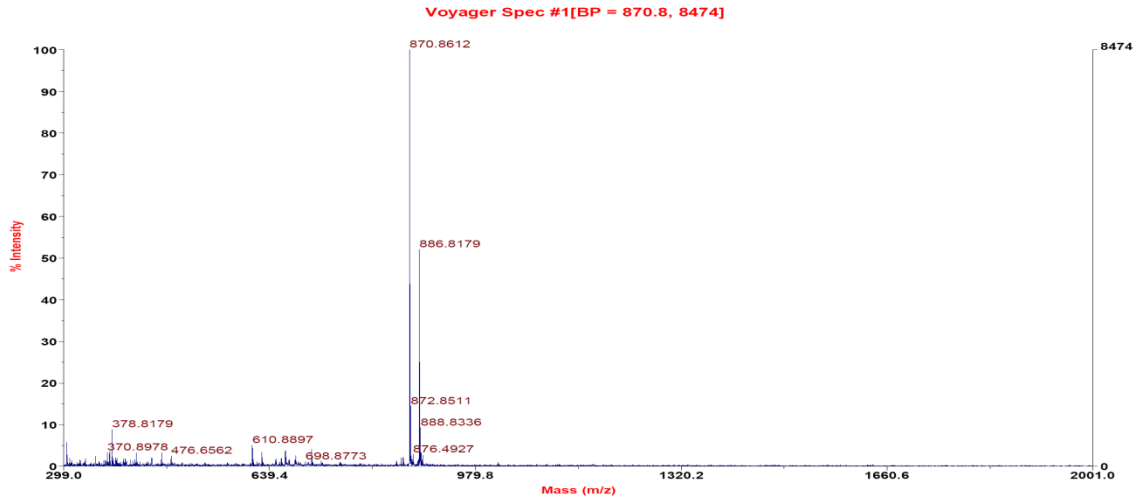


Figure S43. MALDI-TOF spectrum of glycopeptoid (**57-1**)